The vessel was opened in a nitrogen-filled glovebag, the lower portion containing the gray-brown nonvolatile residue was cut off and removed, and the $Sn(CH_3)_2C_2B_4H_4$ (III) was washed with degassed methylene chloride and resublimed at room temperature to produce 50 mg (4% yield) of pure product.

Reaction of $PbBr_2$ with $Na^+[(CH_3)_2C_2B_4H_5]^-$. A 4.0-mmol quantity of the carborane salt in THF was allowed to react with 3.9 mmol of $PbBr_2$ in a procedure identical with the preceding synthesis. Sublimation of $Pb(CH_3)_2C_2B_4H_4$ (IV) from the yellowish-brown residue at room temperature onto a −78 °C cold finger gave 22 mg of light yellow product.

Reaction of $Sn(CH_3)_2C_2B_4H_4$ (III) with $(\eta^5\text{-}C_5H_5)Co(CO)_2$. A "hot–cold" reactor, consisting of a cylindrical Pyrex tube 24 mm in diameter and equipped with a greaseless Teflon stopcock at one end for attachment to the vacuum line, was charged with 1.2 mmol of $Sn(CH_3)_2C_2B_4H_4$ and 1.8 mmol of $(\eta^5\text{-}C_5H_5)Co(CO)_2$. The central portion of the tube was maintained at 150 °C by a Variac-controlled heating tape while the lower end was held at 70 °C in an oil bath. After 24 h the tube was cooled in liquid nitrogen and the noncondensables were removed on the vacuum line. On warming of the system to room temperature the volatile materials were removed by distillation. Extraction of the residue with methylene chloride gave a dark brown solution which was separated by preparative thin-layer chromatography. Development on silica gel plates with a 2:1 chloroform–hexane mixture gave yellow $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ (100 mg, 0.48 mmol, R_f 0.77) identified from its ^{11}B NMR and mass spectra,[13] and dark red $(\eta^5\text{-}C_5H_5)CoSn(CH_3)_2C_2B_4H_4$ (V) (20 mg, 0.06 mmol; R_f 0.58). A trace of $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_4H_4$[12,17] was also obtained and identified from its mass spectroscopic cutoff at m/e 350. The partial decomposition of V to produce $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ was observed during development on silica gel; most of the latter compound could be removed by vacuum sublimation onto a −78 °C cold finger, leaving behind the less volatile V.

The reaction of the same two reagents in refluxing n-nonane at 151 °C under dry nitrogen for 4 h, followed by elution of the dark brown residue on silica gel with hexane, gave $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ but no V was detected.

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Registry No. I, 63181-06-6; II, 63181-05-5; III, 63181-04-4; IV, 63181-03-3; V, 63230-65-9; $Na_2C_2B_5H_7$, 63230-64-8; $Na^+[(CH_3)_2C_2B_4H_5]^-$, 54244-93-8; $Na^+C_2B_4H_7^-$, 63231-39-0; $PbBr_2$, 10031-22-8; GeI_2, 13573-08-5; $SnCl_2$, 7772-99-8; $(\eta^5\text{-}C_5H_5)Co(CO)_2$, 12078-23-8; $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$, 50932-66-6; $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_4H_4$, 63269-89-6.

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Hydrogen–Deuterium Exchange between MBH_4 and MBD_4 (M = Li, Na). Isotope Effects on the ^1H and ^{11}B NMR Spectra of the BH_nD_{4-n} Anions and a Discussion of Exchange Reactions in Some Covalent Tetrahydroborate Systems

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The ^1H NMR spectra of lithium and sodium borohydrides, in various solvents, have been recorded. The resulting chemical shift and coupling constant data do not yield any clear indications of variations in solution structure. Hydrogen–deuterium exchange between $LiBH_4$ and $LiBD_4$ occurs in some ethereal solvents yielding a mixture of partially substituted species, $LiBH_nD_{4-n}$ (n = 0 to 4). These observations are relevant to the isotopic distribution in the products of exchange reactions involving some covalent borohydrides. Isotope effects in the ^1H and ^{11}B NMR spectra of $LiBH_nD_{4-n}$ (THF solvent) and $NaBH_nD_{4-n}$ (alkaline aqueous solvent) are described. Chemical shifts (^{11}B and ^1H) and coupling constants, $J(^{11}B\text{–}H)$, decrease approximately monatonically with deuterium substitution. These isotope effects are considered to arise from the modification of the vibrational characteristics of the $(BH_nD_{4-n})^-$ species.

Introduction

In 1952, Brown and co-workers demonstrated that tritium gas exchanged with the hydrogen in lithium and sodium tetrahydroborates at elevated temperatures.[2] Their method was later extended by Mesmer and Jolly into a convenient preparation for KBD_4, in which the anions BH_3D^-, $BH_2D_2^-$, and BHD_3^- were shown to occur as intermediates.[3] It has since been demonstrated[4] that a mixture of $LiBH_4$ and $LiBD_4$

Table I. Chemical Shifts and Coupling Constant for $LiBH_4$ and $NaBH_4$ in Various Solvents, from ^1H NMR

Compd	Solvent	Molarity	Chem shift, ppm[a]	$J_{^{11}B-H}$, Hz[b]
$LiBH_4$	1. Pyridine	0.2	1.38	81.3[c]
	2. Diglyme[f]	0.3	−0.45	81.2
	3. Monoglyme[g]	1.2	−0.47	81.1
	4. Tetrahydrofuran	0.8	−0.48	81.1
	5. Diethyl ether	0.4	−0.41	81.1[d]
$NaBH_4$	6. D_2O/1.0 N NaOH	0.8		80.6[e]
	7. Pyridine	0.2	1.26	81.3
	8. Diglyme	0.3	−0.47	81.2
	9. Monoglyme	0.2	−0.47	81.0

[a] A positive value indicates a downfield shift with respect to internal TMS. [b] Cf ref 6. [c] Cf 1.27 ppm and 81.0 Hz (ref 12). [d] Cf 75 ± 3 Hz (ref 10). [e] Cf 82 ± 3 Hz (ref 10) and 81 Hz (ref 11). [f] Diglyme = diethylene glycol dimethyl ether, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$. [g] Monoglyme = ethylene glycol dimethyl ether, $CH_3OCH_2CH_2OCH_3$.

readily undergoes H–D exchange at room temperature in tetrahydrofuran, producing a mixture of species $LiBH_nD_{4-n}$ (n = 0–4). Also, isotope effects on the coupling constant and chemical shift were present. Consequently, the $[BH_nD_{4-n}]^-$ system could serve as an excellent source of data on some isotope effects. There had also been reports on intermolecular exchange between $LiBH_4$ and the covalent systems[5,6] $Zr(BH_4)_4$ and $Al(BH_4)_3$. These results prompted us to make a closer examination of MBH_4/MBD_4 solutions (M = Li, Na) in various common solvents, using NMR spectroscopy.

Experimental Section

$LiBH_4$ and $LiBD_4$ (98% isotopic purity) were obtained from Koch Light Co. Both were purified prior to use (largely unnecessary for fresh samples) by dissolving in dried diethyl ether, filtering, then removing ether solvent by extended evacuation on a vacuum line. $NaBH_4$ and $NaBD_4$ were obtained from Research Organic/Inorganic Chemical Corp. Apart from drying on a vacuum line, both were used without further purification.

All organic solvents were dried by refluxing and distilling over calcium hydride under an atmosphere of nitrogen and were subsequently degassed by successive freeze–thaw cycles on a vacuum line. Solutions were made up in a nitrogen-filled Mecaplex AG. glovebox and filtered through diatomaceous earth (predried by extended evacuation) prior to NMR measurements. In the survey of H–D exchange reactions, solutions of the hydridoborate were added to deuterioborate solutions such that the BH_4^-/BD_4^- ratios correspond approximately to 60% H, 40% D. Survey ^1H NMR spectra (23.5 kG, 100 MHz) were recorded on a JEOL MH 100 spectrometer and accurate data on a JEOL PS 100 instrument internally locked on solvent resonances. ^{11}B NMR spectra (23.5 kG, 32.09 MHz) were recorded on the PS 100 instrument with modifications based on those described elsewhere.[7] In the ^1H and ^{11}B NMR studies of $NaBH_nD_{4-n}$ mixtures, 1.0 N NaOH/D_2O and 1.0 N NaOH/H_2O solvents, respectively, were employed, with solutions approximately 1.5 M in boron. The sodium hydroxide was present to reduce the rate of hydrolysis.[8] In the studies of the ^1H and ^{11}B NMR of $LiBH_nD_{4-n}$, solutions were approximately 2 M in boron.

Results and Discussion

(1) The BH_4^- Ion. The ^1H NMR spectrum of the BH_4^- ion consists of an intense quartet due to ^1H–^{11}B coupling (^{11}B: $I = {}^3/_2$, natural abundance 80.4%) superimposed on a weaker septet due to ^1H–^{10}B coupling (^{10}B: $I = 3$, natural abundance = 19.6%). The corresponding ^{11}B NMR spectrum is a 1:4:6:4:1 quintet arising from coupling to four equivalent protons.[9] Published data on solution NMR studies of alkali metal tetrahydroborates are relatively sparse and have been derived largely from ^{11}B NMR spectroscopy.[6,10-13] Proton NMR chemical shifts and coupling constants obtained in this work for $LiBH_4$ and $NaBH_4$ in various solvents are given in Table I.

Table II. Results of H-D Exchange Experiments in Solution

Compd	Solvent	Exchange result
$LiBH_4$	1. Pyridine	−
	2. Diglyme	+
	3. Monoglyme	+
	4. Tetrahydrofuran	+
	5. Diethyl ether	+
$NaBH_4$	6. D_2O/1 N NaOH	−
	7. Pyridine	−
	8. Diglyme	−
	9. Monoglyme	−

In all cases, $J(^{11}B\text{-}H) = 81.0 \pm 0.4$ Hz and the small observed variations are not statistically significant. These data compare with an often-quoted earlier result[10] in which $J(^{11}B\text{-}H)$ for $LiBH_4$ (in diethyl ether) and $NaBH_4$ (in water) were estimated as 75 ± 3 and 82 ± 3 Hz, respectively. All the measured coupling constants $J(^{10}B\text{-}H)$ are in the range 27.05 to 27.25 Hz, consistent with the value calculated from $(\gamma^{10}B/\gamma^{11}B)J(^{11}B\text{-}H)$, within experimental error. The proton chemical shifts of both $LiBH_4$ and $NaBH_4$ in ethereal solvents (systems 2 to 5, 8, and 9 in Table I) are relatively insensitive to both solvent and cation. All lie within the range 0.45 ± 0.04 ppm to high field of TMS. The exceptionally low field resonance positions of lithium and sodium tetrahydroborate in pyridine may derive from ring current shifts. It has been known for some time that in diethyl ether and THF, $LiBH_4$ suffers a considerable degree of association[14] and detailed studies of structure in these solvents have recently been published.[15,16] Further, Shirk and Shriver[17] have noted variations in the Raman spectral characteristics of systems 1 to 9 which may be indicative of structural differences in solution. What little variation we do find in the current NMR data, however, does not seem to be readily correlated with the Raman results, nor of itself, to give any clear indication of solution structure.

(2) Exchange. The results of a survey of the occurrence of H–D exchange between MBH_4 and MBD_4 (M = Li, Na) in the solvent systems 1 to 9 are presented in Table II. Positive results were gained only when $LiBH_4$ and $LiBD_4$ were mixed in ethereal solvents.[18] In order for exchange to take place, B–H bond cleavage must occur in some manner, plausibly through a concerted mechanism of the form:

$$Li^+ + BH_4^- + BD_4^- \rightleftharpoons Li^+ + H^- + BH_3BD_4^-$$

in which the lithium ion acts as an intermediary facilitating the juxtaposition of anionic species and subsequent H–D interchange. The existence of the ion $BH_3BH_4^-$ has been established,[19,20] and Ashby and co-workers[15,16] have proposed the occurrence of the species $[Li(BH_4)_2]^-$ (and perhaps higher aggregates) in THF and diethyl ether solutions of $LiBH_4$. It is interesting that the Raman characteristics of a pyridine solution of $LiBH_4$, in contrast to ethereal solutions, give no evidence of strong $Li^+BH_4^-$ association.[17] It is plausible, then, that the conspicuous absence of H–D exchange between $LiBH_4$ and $LiBD_4$ in pyridine may reflect a distinction in solution structure.

It was apparent from the ^1H and ^{11}B NMR spectra from $LiBH_4/LiBD_4$ mixtures in THF[4] that not only did H–D exchange take place but also isotope effects on the coupling constant and chemical shift were present.[21] Since isotope effects had not been widely documented in boron systems,[22] the availability of the various $[BH_nD_{4-n}]^-$ anions made an ideal opportunity for their investigation. Two systems have therefore been studied in detail. The series $LiBH_nD_{4-n}$ in THF is attractive because of the high solubility. In addition to solubility considerations, $NaBH_nD_{4-n}$ dissolved in (alkaline) H_2O or D_2O is particularly facile in that very narrow line widths are readily attainable.

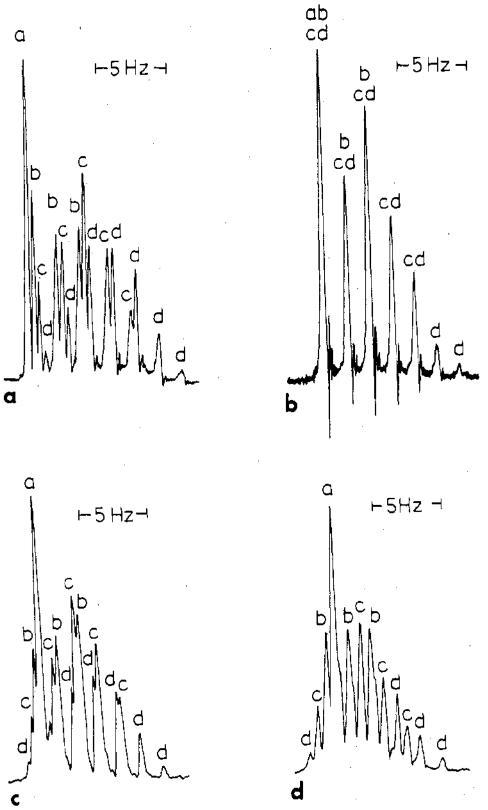

Figure 1. The four major features a, b, c and d (in order, low to high field) of the ^1H NMR spectrum of a mixture of species $NaBH_nD_{4-n}$ (n = 0 to 4) in 1.0 M $NaOH/D_2O$ solvent. The designations (a) BH_4^-, (b) BH_3D^-, (c) $BH_2D_2^-$, (d) BHD_3^-, and (e) BD_4^- are also used in other figures. Consecutive members of this quartet of multiplets are separated by $J(^{11}B\text{-}H) \sim 81$ Hz. The weaker septet multiplets due to $^{10}B\text{-}H$ coupling is not shown.

(3) Proton NMR Spectra. The ^1H NMR spectrum of a mixture of species $NaBH_nD_{4-n}$ (Figure 1) appears as four major complex features separated by approximately 81 Hz, $J(^{11}B\text{-}H)$. Each feature consists of a superposition of signals whose multiplicity arises from H–D coupling. For simplicity, the four major spectral features will be referred to as "features a, b, c, and d" going from low to high field.

Within each feature, components due to BH_4^- (singlet), BH_3D^- (1:1:1 triplet), $BH_2D_2^-$ (1:2:3:2:1 quintet), and BHD_3^- (1:3:6:7:6:3:1 septet) are observed.

That an isotope shift is operative is apparent from Figure 1 since in each of the features a, b, c, and d the centers of the component BH_4^- (a), BH_3D^- (b), $BH_2D_2^-$ (c), and BHD_3^- (d) multiplets occur to successively higher field. However, it is also starkly apparent that the four features a, b, c, and d are not identical, and indeed the above separations can be seen to decrease in a stepwise fashion in passing from a to d. This derives from a decrease in the absolute magnitude of $J(^{11}B\text{-}H)$ from a maximum in BH_4^- to a minimum in BHD_3^-. The proton chemical shifts of $NaBH_nD_{4-n}$ decrease (i.e., shift upfield) by about 0.0146 ppm per deuterium substitution and and $J(^{11}B\text{-}H)$ decreases by about 0.37 Hz per replacement. Relevant data are given in Table III and Figures 2a and 2b. It should be noted that this system is particularly well suited to the detection of an isotope effect on a coupling constant, in that the separation between the centers of, for example, the BH_4^- and BH_3D^- multiplets in features a and d differ by $3x[J(^{11}B\text{-}H), BH_4^- - J(^{11}B\text{-}H), BH_3D^-]$. In all isotopic variants, a coupling constant $^2J(H\text{-}D) = 1.61$ Hz (standard deviation = 0.03 Hz) was observed, and indeed any isotope effect on $^2J(H\text{-}D)$ would be expected to be small.[23] This value compares with $^2J(H\text{-}D)$ estimated as 1.90 and 1.78 Hz for CH_nD_{4-n} and $(NH_nD_{4-n})^+$, respectively.[24,25] In the absence of a primary isotope effect, $^2J(H\text{-}H)$ can be calculated from $(\gamma H/\gamma D)J(H\text{-}D) = 10.5$ Hz.

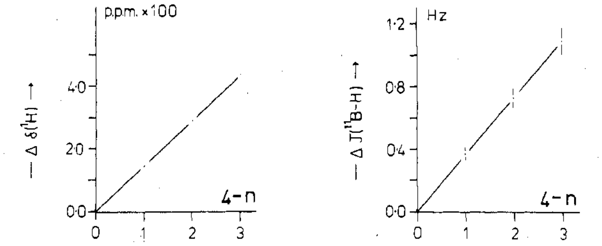

Figure 2. Isotope effects for $NaBH_nD_{4-n}$ as a function of the number of D substituents ($4 - n$), from ^1H NMR: (a) proton chemical shifts; (b) coupling constant, $J(^{11}B\text{-}H)$. Chemical shifts and coupling constants decrease with increasing D substitution.

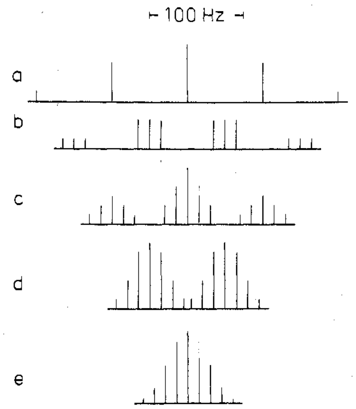

Figure 3. The patterns of line in the ^{11}B NMR due to: (a) BH_4^- (1:4:6:4:1); (b) BH_3D^- (1:1:1, 3:3:3, 3:3:3, 1:1:1); (c) $BH_2D_2^-$ (1:2:3:2:1, 2:4:6:4:2, 1:2:3:2:1); (d) BHD_3^- (1:3:6:7:6:3:1, 1:3:6:7:6:3:1); (e) BD_4^- (1:4:10:16:19:16:10:4:1). In Figures 4 to 6, the centers of resonances (a) to (e) occur successively to higher field.

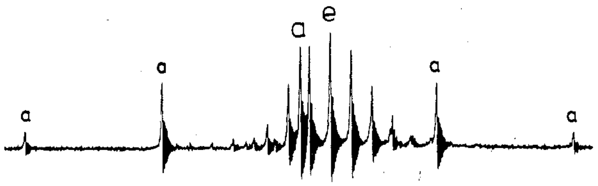

Figure 4. The ^{11}B NMR spectrum of a mixture of $NaBH_4$ (a) and $NaBD_4$ (e) in 1.0 M $NaOH/H_2O$. H–D exchange is absent. The center of the BD_4^- resonance occurs upfield of the center of the BH_4^- resonance. Features due to $NaBHD_3$ impurity in the $NaBD_4$ sample are weakly visible.

The ^1H NMR spectra of $LiBH_nD_{4-n}$ mixtures[4] show evidence of similar isotope effects on chemical shifts and coupling constants, but the greater line widths of component peaks make it difficult to gain as much or as accurate data. It is estimated that the BH_3D^- resonance occurs about 0.011 ppm upfield of the BH_4^- resonance, that $J(^{11}B\text{-}H)$ for BH_3D^- is approximately 0.4 Hz less than $J(^{11}B\text{-}H)$ for BH_4^-, and that $^2J(H\text{-}D)$ for $BH_3D^- = 1.6$ Hz. These values are compatible, within the limitations of measurement, with the $NaBH_nD_{4-n}$ results. We have also found that, within experimental error, the relevant peak positions are invariant over a temperature range of −35 to +58 °C. Thus the rate of H–D exchange is slow on the NMR time scale and does not significantly affect spectral characteristics.

(4) Boron-11 NMR Spectra. In Figure 3 the patterns of lines due to BH_4^- (a), BH_3D^- (b), $BH_2D_2^-$ (c), BHD_3^- (d), and BD_4^- (e) in the ^{11}B NMR are illustrated. The spectrum of a mixture of $NaBH_4$ and $NaBD_4$ in alkaline aqueous solution (no H–D exchange) shown in Figure 4 clearly demonstrates the presence of a considerable isotope effect on ^{11}B

Table III. Isotope Effects in the ^1H and ^{11}B NMR Spectra of MBH_nD_{4-n} (M = Li, Na; n = 0 to 4)[a]

Compd	n	^1H NMR $10^2\Delta\delta$, ppm	^{11}B NMR $\Delta\delta$, ppm	^1H NMR $\Delta J(^{11}B-H)$, Hz	^{11}B NMR $\Delta J(^{11}B-H)$, Hz
$LiBH_nD_{4-n}$	4	0.0	0.0	0.0	0.0
	3	1.1	0.139 (0.007)	0.4	0.45 (0.22)
	2		0.275 (0.005)		0.55 (0.13)
	1		0.423 (0.009)		1.09 (0.26)
	0		0.558 [0.004]		
$NaBH_nD_{4-n}$	4	0.0	0.0	0.0	0.0
	3	1.46 (0.02)	0.137 (0.004)	0.37 (0.02)	0.68 (0.25)
	2	2.90 (0.03)	0.271 (0.004)	0.73 (0.03)	0.71 (0.22)
	1	4.41 (0.05)	0.411 (0.004)	1.09 (0.04)	1.02 (0.20)
	0		0.543 [0.007]		

[a] $\Delta\delta$ = isotope shift upfield of BH_4^-. $\Delta J(^{11}B-H) = [J(^{11}B-H), BH_4^- - J(^{11}B-H), BH_nD_{4-n}^-]$. Where ten or more measurements were made, calculated standard deviations are given in parentheses. Where less than ten measurements were made, an average deviation is given in square brackets.

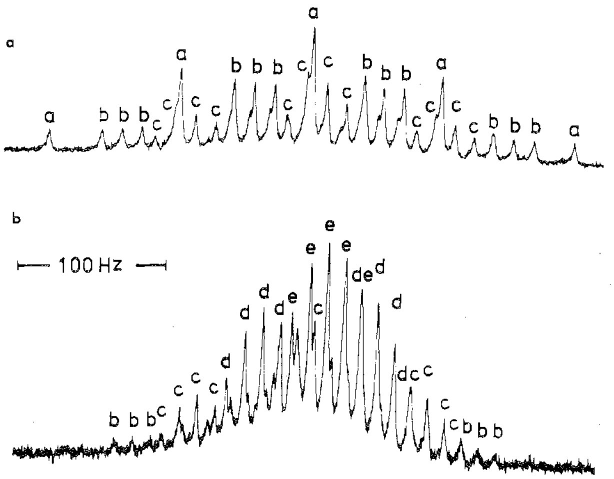

Figure 5. The ^{11}B NMR spectra of $LiBH_4/LiBD_4$ mixtures in THF in which H–D exchange has occurred: (a) BH_4^-, BH_3D^-, and $BH_2D_2^-$ species predominate; (b) $BH_2D_2^-$, BHD_3^-, and BD_4^- predominate.

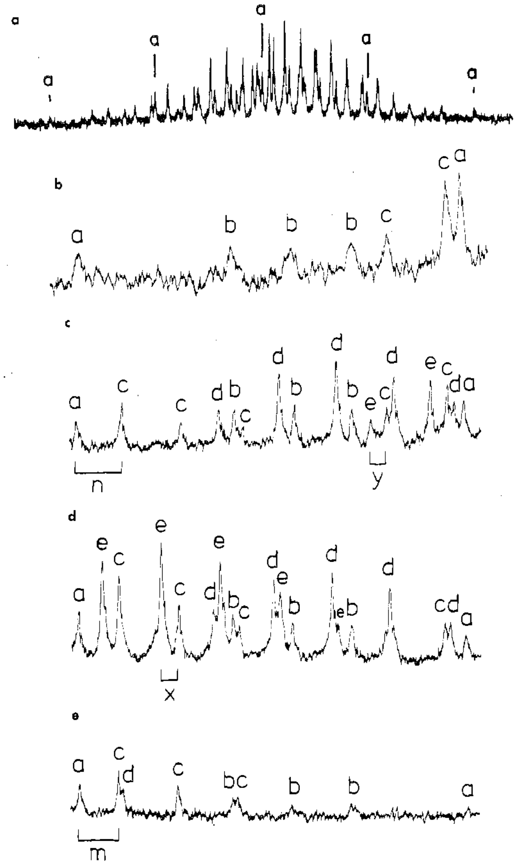

Figure 6. The ^{11}B NMR spectrum of a mixture of species $NaBH_nD_{4-n}$ dissolved in 1.0 M $NaOH/H_2O$. Figures 6b–e are expansions of the regions between the components of the BH_4^- quintet shown in Figure 6a. Most of the 55 expected lines (Figure 3) are observed. Not all observed resonances are labeled in Figure 6. The separation between adjacent lines due to BH_4^- (a) is 81 Hz.

chemical shifts. From Figure 5 ($LiBH_nD_{4-n}$) and Figure 6 ($NaBH_nD_{4-n}$) it is found that the centers of the ^{11}B NMR signals of the component species occur at successively higher fields with increasing deuteration. The effect is approximately linear with n, corresponding to an upfield shift of about 0.14 ppm per deuterium substituent, in both the lithium and the sodium systems.

The isotope effects on $J(^{11}B-H)$, which were accurately measured from ^1H NMR spectra of $NaBH_nD_{4-n}$, may also be deduced from the ^{11}B NMR data. For example, the separations denoted m and n in Figure 6 differ by $2x[J(^{11}B-H), BH_4^- - J(^{11}B-H), BH_2D_2^-]$. Such measurements for the $NaBH_nD_{4-n}$ mixtures yield results comparable with the ^1H NMR data but are of poorer precision. Hence, while it was not possible to measure the full range of isotope effects on $J(^{11}B-H)$ for the $LiBH_nD_{4-n}$ system from ^1H NMR spectra, these data have been deduced from the ^{11}B NMR spectra, and the results are comparable with those for $NaBH_nD_{4-n}$.

Secondary isotope effects on coupling constants $J(^{11}B-D)$ may be sought from, for example, the differences between the separations marked x and y in Figure 6, which would be expected to be $4x[J(^{11}B-D), BH_2D_2^- - J(^{11}B-D), BD_4^-]$. Within experimental error, however, all such distances are found to be equal and it is estimated that the $J(^{11}B-D)$ values for $BH_2D_2^-$ and for BD_4^- differ by less than 0.2 Hz. $J(^{11}B-D)$ is estimated as 12.2 Hz (standard deviation 0.2 Hz) for $NaBH_nD_{4-n}$ and 12.3 Hz (standard deviation 0.2 Hz) for $LiBH_nD_{4-n}$, both of which are consistent with the value calculated from $(\gamma D/\gamma H)J(^{11}B-H)$.

Isotope effect data from the present work are summarized in Table III. That deuterium substitution produces upfield shifts in the ^1H and ^{11}B NMR is in keeping with the majority of observations for various isotope replacements and for various resonant nuclei.[26-28] The current ^1H NMR results contrast with the earlier report[3] for aqueous KBH_nD_{4-n}, in which upfield shifts of 0.02 and 0.04 ppm for n = 3 and 2, respectively, were deduced, and no effect on $J(^{11}B-H)$ was detected.[29] The present ^{11}B NMR results compare with an earlier report[30] for deuterated sodium borohydrides in which the ^{11}B signals of BH_3D^- and BD_4^- were reported to occur 0.17 ± 0.03 and 0.58 ± 0.04 ppm to high field of the BH_4^- resonance. However, the sample investigated in the latter work would not have facilitated the observation of the relatively small effect on $J(^{11}B-H)$. That the ^{11}B isotope shift is about ten times that observed for proton resonances reflects the approximately tenfold wider chemical shift range apparent[10,11,31,32] in ^{11}B NMR.

Relatively few observations of secondary isotope effects on coupling constants are available for comparison with the present results.[33-39] While, in most cases, substitution of D for H produces a decrease in J(X–H), consistent with the $BH_nD_{4-n}^-$ data, some increases have also been reported.[36] The magnitude of the effect has been found to vary from zero (e.g., $(C_6H_5)_2SnH_2$, J(Sn–H) = 1930.0 ± 1 Hz; $(C_6H_5)_2SnHD$, J(Sn–H) = 1929.7 ± 1 Hz, ref 37) to a few hertz. The present results are comparable with, for example, a recent estimate[38] that $J(^{13}C\text{–}H)$ for $C_6H_5{}^{13}CH_3$ is slightly greater than $J(^{13}C\text{–}H)$ in $C_6H_5{}^{13}CH_2D$ by 0.6 ± 0.4 Hz.

That there is such a marked similarity between the results obtained from $LiBH_nD_{4-n}$ in THF and those from $NaBH_nD_{4-n}$ in aqueous solution suggests that the observed effects are unlikely to have been grossly affected either by solvent–solute interactions or by cation–anion association in solution. The effects are therefore considered to arise from the modification of (intramolecular) vibrational characteristics on deuteration.

Isotope effects in diatomics, such as the isotopic variants of the hydrogen molecule[40-43] have been treated in detail. It is well established that contributions from modifications of both harmonic and anharmonic contributions to the vibrational energy may be significant and even of opposite sign. By contrast, a number of attempts which have been made to explain the observations for polyatomic molecules (ref 26, 28, and references therein) have been based on rather simple models. In view of this current state of theory, further rationalization of the present data does not seem warranted at this time.

Molecular reorientation of three-coordinate or distorted four-coordinate boron compounds (in which there is significant coupling between the electric field gradient and boron nuclear quadrople) will generally provide an efficient mechanism for the nonradiative relaxation of ^{11}B nuclear spin. This results in the broadening of both ^{11}B NMR signals and the ^{1}H NMR signals of protons coupled to the boron nuclei.[44] Since the isotope effects observed in both ^{11}B and ^{1}H NMR spectra are relatively small in magnitude, it would seem unlikely that such isotope effects will be readily detected in any but the most symmetrical boron compounds in which the electric field gradient at the boron nucleus is minimal. To this extent, the tetrahedral (or near tetrahedral) BH_4^- (and substituted) ions are particularly suitable. Accordingly, we feel this work represents not only a worthwhile addition to the available data pertaining to secondary isotope effects but also represents the most complete record of such effects in the ^{1}H and ^{11}B NMR of a boron compound.

(5) Extension to Covalent Systems. Although intramolecular exchange of hydrogen atoms is well-known in covalent hydroborate systems,[45] the existence of intermolecular exchange between $LiBH_4$ (or $LiBD_4$) and covalent zirconium borohydride was only clearly established in 1970 by Wallbridge and co-workers.[5] A mechanism for the exchange between $LiBD_4$ (or $LiBH_4$) and $Zr(BH_4)_4$ in diethyl ether was proposed as follows:

$$\mathrm{Li^{*}BH_4 + Zr(BH_4)_4 \rightleftharpoons \underset{A}{Li[Zr(BH_4)_4{}^{*}BH_4]} \rightleftharpoons LiBH_4 + Zr(BH_4)_3{}^{*}BH_4} \tag{1}$$

An intermediate analogous to that marked A above had been suggested[46] for the system $LiBH_4/Al(BH_4)_3$/diethyl ether, and compounds of this type have since been isolated and characterized.[6,47-50] For the $LiBD_4/Zr(BH_4)_4$/diethyl ether system, a mechanism totally represented by eq 1 would result in the species $LiBH_4$, $LiBD_4$, and $Zr(BH_4)_n(BD_4)_{4-n}$ (n = 0 to 4) where discrete BH_4^- and BD_4^- entities remain intact. The possibility of a scrambled isotopic distribution was put forward but not asserted.[5] Further evidence by Ehemann and Nöth[47] suggested that the equilibrium

$$\mathrm{LiBH_4 + Zr(BH_4)_4 \rightleftharpoons LiZr(BH_4)_5}$$

lies to the left at room temperature but strongly to the right at −78 °C. It was also suggested that mechanism 1 might be extended by reactions of the sort

$$\mathrm{LiZr(BH_4)_5 + B' \rightleftharpoons LiZr(BH_4)_5B' \rightleftharpoons LiZr(H)(BH_4)_4 + B'BH_3} \tag{2}$$

where B′ is a Lewis base, here BH_4^- or diethyl ether. Such a scheme presents a situation whereby the hydrogen/deuterium could be randomized in the product molecules.

Since the evidence suggests that in the reactions described in (1) $LiBH_4$ and $LiBD_4$ should coexist in solution, the observation of facile isotope exchange in $LiBH_4/LiBD_4$ systems is of relevance and indicates that reactions of type 3 must be

$$\mathrm{LiBH_4 + LiBD_4 \rightleftharpoons LiBH_3D + LiBD_3H,\ etc.} \tag{3}$$

added to eq 1. Consequently a scrambled H/D distribution is to be expected in the reaction between $LiBD_4$ and $Zr(BH_4)_4$ yielding products $LiBH_nD_{4-n}$ (n = 0 to 4) and $ZrB_4H_mD_{16-m}$ (m = 0 to 16). Reactions between $Al(BH_4)_3$ and a number of compounds LiX (X = H, D, Cl, BH_4) have also been reported[6,46,51] and similar results might be expected for X = BD_4. It is probable that (1) and (3) do not represent the only exchange reactions occurring in solutions of $LiBD_4/Zr(BH_4)_4$ and (2) remains plausible. A mechanism incorporating either an intramolecular proton rearrangement or an intermolecular process involving borane intermediates, $[BH_3]$, has been put forward[51] to explain the isotopic distribution in the products of the reaction between LiD and $Al(BH_4)_3$ in ether.

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Registry No. $LiBH_4$, 16949-15-8; $NaBH_4$, 16940-66-2; $LiBH_3D$, 53538-47-9; $LiBH_2D_2$, 53538-48-0; $LiBHD_3$, 62860-09-7; $LiBD_4$, 15246-28-3; $NaBH_3D$, 20492-86-8; $NaBH_2D_2$, 62816-02-8; $NaBHD_3$, 20492-87-9; $NaBD_4$, 15681-89-7.

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other batches of solvent, the original results were found to be irreproducible. It is conceivable that the exchanged samples arose because of catalysis by an impurity (e.g., peroxides or alcohols) in the original diglyme sample. Although exchanged samples could have been gained from alternative sources, the mixtures of $NaBH_nD_{4-n}$ obtained from these preliminary experiments proved more than adequate sources of spectral information.

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Nature of Alkyl–Hydrogen Exchange Reactions Involving Aluminum and Zinc. 2. Reaction of $(CH_3)_2Zn$ with $LiAlH_4$ in Tetrahydrofuran

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When $(CH_3)_2Zn$ was added to a THF solution of $LiAlH_4$ in 2:1, 3:2, and 1:1 molar ratios, $LiZn_2(CH_3)_4AlH_4$ and $LiZn(CH_3)_2AlH_4$ were formed according to eq 1–3. When the order of addition was reversed and $LiAlH_4$ was added to a THF solution of $(CH_3)_2Zn$ in 1:1, 2:3, and 1:2 molar ratios, $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ were again formed according to eq 1–3. Infrared and ^1H NMR spectroscopic studies, as well as ebullioscopic molecular weight measurements, were used to define the solution composition of the products obtained from these reactions. The role of $LiZn(CH_3)_2AlH_4$ as the intermediate involved in the formation of ZnH_2 from the reaction of $LiAlH_4$ with $(CH_3)_2Zn$ is discussed in light of the spectroscopic studies carried out on this reaction.

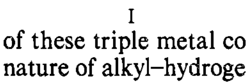
$$2(CH_3)_2Zn + LiAlH_4 \rightleftharpoons LiZn_2(CH_3)_4AlH_4 \qquad (1)$$

$$3(CH_3)_2Zn + 2LiAlH_4 \rightleftharpoons LiZn_2(CH_3)_4AlH_4 + LiZn(CH_3)_2AlH_4 \qquad (2)$$

$$(CH_3)_2Zn + LiAlH_4 \rightleftharpoons LiZn(CH_3)_2AlH_4 \qquad (3)$$

Introduction

Recently we reported the first synthesis of triple metal ate complexes involving an alkali metal, zinc, and aluminum, i.e., $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$.[1] These compounds were formed by the reaction of AlH_3 with $LiZn(CH_3)_2H$ and $LiZn_2(CH_3)_4H$ in THF and are believed to have the structures represented by I and II. In that report we noted that a study of these triple metal complexes could provide clues as to the nature of alkyl–hydrogen exchange reactions between zinc and aluminum.



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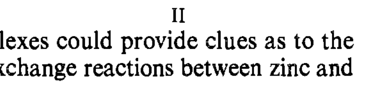

II

In this paper we will report on the formation of $LiZn(CH_3)_2AlH_4$ and $LiZn_2(CH_3)_4AlH_4$ by reaction of $(CH_3)_2Zn$ with $LiAlH_4$ in THF under a variety of conditions. The fact that the triple metal complex, $LiZn(CH_3)_2AlH_4$, can be prepared by allowing $LiAlH_4$ to react with $(CH_3)_2Zn$ offers the first indication of what could be the intermediate involved in the formation of ZnH_2 from these two reagents in diethyl ether.[2] An infrared spectral study of the reaction between $(CH_3)_2Zn$ and $LiAlH_4$ in THF does indeed provide evidence that $LiZn(CH_3)_2AlH_4$ is involved.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[3] Filtrations and other manipulations were carried out in a glovebox equipped with a recirculating system.[4]

Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. Solutions were run in matched 0.10-mm path length NaCl or KBr cells. X-ray powder data were obtained on a Philips-Norelco x-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to x rays for 6 h. The *d* spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer with a standard variable-temperature unit. Ebullioscopic molecular association studies were carried out in THF