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Preliminary communication

SYMMETRICAL EXCHANGE OF POTASSIUM TRIALKYLBOROHYDRIDES WITH TRIALKYLBORANES, DIRECT OBSERVATION OF STERIC EFFECTS BY ^{11}B NMR SPECTROSCOPY

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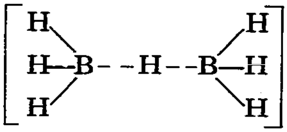
Summary

Mixtures of potassium triethylborohydride and triethylborane in tetrahydrofuran at 25° C show evidence by ^{11}B NMR and IR spectroscopy of essentially quantitative formation of a hydride bridged diborohydride ion and of rapid exchange between diboron and monoboron species. The formation of an association compound (2/1) and the rate of hydride exchange is remarkably sensitive to increases in steric hindrance of the alkyl groups on boron.

Formation of 2/1 addition compounds from trialkylboranes and saline hydrides (MH, M = Li, Na, or K) have been observed in direct reaction of the components in ether solvents [1]. The resulting hexaalkyldiborohydride species appear to possess hydride bridged structures similar to that of the parent diborohydride ion (I, (B_2H_7)) [2].



(I)

The diborohydride ion is reported to undergo rapid exchange with diborane [2b] but only slow exchange with borohydride ion [2b,e]. Unfortunately, no such comparable studies with trialkylborohydrides have been reported. Recently, a variety of potassium trialkylborohydrides with alkyl groups of increasing steric requirements have been prepared [3]. Consequently, it was of interest to examine the interaction between potassium trialkylborohydrides and trialkylboranes by IR and ^{11}B NMR.

The ^{11}B NMR spectrum of potassium triethylborohydride exhibits a sharp

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*Dedicated to Professor Herbert C. Brown in recognition of his contributions to chemistry.

doublet at —13.0 (J(B—H) 68 Hz). It has a strong B—H absorption in IR at 2020 cm^{-1}. Addition of one equivalent of triethylborane to a tetrahydrofuran solution of potassium triethylborohydride results in a strongly exothermic reaction accompanied by changes in the ^{11}B and IR spectra (Table 1) clearly indicating the formation of the bridged ion. Addition of even a trace of triethylborane to a sample of potassium triethylborohydride results in the collapse of the doublet to a singlet due to exchange.

TABLE 1

SPECTRAL CHARACTERISTICS OF POTASSIUM TRIETHYLBOROHYDRIDE—TRIETHYLBORANE SYSTEM

Samples[a]	IR ν(B—H) (cm^{-1})	^{11}B NMR[b]	
		δ (ppm)	J(B—H) (Hz)
KEt_3BH	2020 (br)	—13.0	68
KEt_3BH + 0.4 BEt_3		— 0.5	
KEt_3BH + 1.0 BEt_3B	1940 (v br)[c]	+ 7.5[d]	
KEt_3BH + 2.0 BEt_3B	1940 (v br)	+33.0	
BEt_3		+78.0	

[a] Solution in THF, prepared and transferred under argon. Total boron concentration 0.6—1.5 *M*. [b] Values of δ relative to $BF_3{:}Et_2O$ (external) = 0. Spectra were measured using external $(MeO)_3B$ references, calibrated to $BF_3{:}Et_2O$ and converted. [c] Ref. 1b reports for the lithium analog in diglyme 1915 cm^{-1}. [d] Ref. 1c reports for the intermolecular bridged hydride formed from KH and $(CH_2)_4B(CH_2)_4(CH_2)_4$ to be δ + 6.7 ppm. Coupling of bridging hydrogen was not observed in this case also.

Mixtures of various ratios of triethylborane and potassium triethylborohydride produced ^{11}B resonances whose position corresponded to the average signals of the association compound and triethylborane or triethylborohydride, whichever was in excess, and indicated an overall association constant of > 50 (eq. 1 and 2). There are chemical manifestations of formation of the bridged ion

$$KEt_3BH + Et_3B \xrightarrow[25^\circ C]{THF} K[Et_3B\text{ - - - }H\text{ - - - }BEt_3] \qquad (1)$$

$$K[Et_3B\text{ - - - }H\text{ - - - }BEt_3] + KEt_3BH \text{ (or) } Et_3B \rightarrow \text{Rapid exchange} \qquad (2)$$

as well: n-decyl chloride, which is reduced rapidly by potassium triethylborohydride, reacts very sluggishly with hexaethyldiborohydride.

Further, our preliminary studies clearly indicate that the formation of a 2/1 addition compound and hydride exchange is remarkably sensitive to the steric requirements of the alkyl substituent on boron. For example, the behavior of n-Bu_3B, i-Bu_3B, and s-Bu_3B with the corresponding potassium trialkylborohydrides exhibits remarkable differences. Each of these three trialkylborohydrides exhibits a clean doublet in the range δ —7 to —16 ppm.

Addition of one mole of n-Bu_3B to the THF solution of K-n-Bu_3BH causes the doublet to collapse into a singlet, in the manner previously described for the ethyl system.

On the other hand, addition of one mole of i-Bu_3B to the solution of K-i-Bu_3BH causes the doublet to collapse completely into the background, with no absorption visible.

Finally, the addition of one mole of s-Bu_3B to K-s-Bu_3BH has no effect on the ^{11}B spectrum the doublet remains essentially unaltered.

These results can readily be accounted for in terms of the effect of the steric requirements of R_3B on the rate of exchange with the trialkylborohydride (eqn. 3).

$$KR_3B^{\star}H + R_3B \rightleftharpoons R_3B^{\star} + R_3BHK \qquad (3)$$

In the tri-n-butyl system, the rate of exchange is rapid compared to the NMR time scale and the doublet is converted into the singlet. In the triisobutyl system, the rate of exchange is slower, comparable to that of the NMR time scale, and the peak collapses. In the tri-s-butyl system, the rate of exchange is slow compared to the NMR time scale and the doublet is not altered.

These preliminary results reveal a remarkable sensitivity of the rate of the exchange reaction to the steric requirements of the trialkylborane species and establishes the unique ability of ^{11}B NMR to examine these phenomena. We are currently pursuing investigations of such exchange phenomena in detail.

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