causes $\Delta V°$ to increase while $\Delta H°$ approaches zero, and $(\Delta V° - \beta\Delta H°/\rho c_p)$ remains roughly constant.

The question must now be answered as to why the observed kinetic behavior is markedly different in CCl_4–DMSO compared to $CHCl_3$–DMSO. Obviously the difference must be due to the relative hydrogen bonding capabilities of chloroform and carbon tetrachloride. Chloroform is known to form weak hydrogen bonds;[3] *e.g.*, the association constant between DMSO and chloroform in carbon tetrachloride has been estimated to be 31 M^{-1}.[17] This accounts for the lower stability of the dimer in chloroform relative to carbon tetrachloride. The differences in kinetic behavior in CCl_4–DMSO and $CHCl_3$–DMSO, imply that the breakdown and formation of a DMSO–2-pyridone hydrogen bond in the dimer is more rapid in chloroform than in carbon tetrachloride. This is probably due to the fact that this step is facilitated by simultaneous formation or breakdown of a hydrogen bond between DMSO and chloroform.

The pertinence of these models to biological processes is, of course, an open question. This work shows that solvation–desolvation processes can become rate limiting in hydrogen bond formation and breakdown. However, in this particular case a quite inert environment is required. Conceivably, hydrophobic pockets in proteins might provide such an environment. Rate constants for desolvation in water of molecules containing hydrophobic groups have been measured,[18] and are $\sim 10^8$ sec^{-1}, similar to the corresponding rate constants reported here. Thus this work may be of relevance in understanding biological processes. In any event, the mechanism of hydrogen-bonded dimerization has now been studied in a variety of solvent systems and can be understood in terms of the underlying elementary steps.

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Communications to the Editor

Preparation of Lithium Nonahydrotetraborate

Sir:

Pentaborane(9),[1-3] hexaborane(10),[4,5] and decaborane(14)[6-8] have been shown to be Brønsted acids. The acid hydrogen atoms in these boranes occupy bridge positions. Shore, *et al.*,[4,5] have shown that the Brønsted acidity decreases in the order $B_{10}H_{14} > B_6H_{10} > B_5H_9$. The relative acidity of the hydrogen atoms in diborane(6)[9-14] is still in doubt. Kodama[15] found that ether solutions of tetraborane(10) absorbed ammonia reversibly at low temperature and suggested that addition was on bridge positions. In the present study we confirm this suggestion and show that tetraborane(10) is a Brønsted acid and that the acid hydrogen atom occupies a bridge position.

Ether solutions of methyllithium and tetraborane(10) were condensed together in a tube at −196°. The tube was sealed and warmed to −78°. A moderate amount of bubbling took place and the reaction was complete after 90 min. The tube was opened and the material volatile at −196° was shown to be pure methane by its infrared spectrum and its −196° vapor pressure (10.0 Torr). Reaction yields were calculated by taking the ratio (millimoles of methane produced)/(millimoles of tetraborane(10) used). The molar excess of methyllithium varied from 0 to 2 *M*. Fourteen reactions yielded amounts of methane corresponding to 78–98% of the theoretical. The average yield for the 14 reactions was 89.5%. Optimum yields were obtained when no less than a 20% excess of methyllithium was used and when the initial 2.3 *M* methyllithium solution in ethyl ether was diluted with no less than a 40% additional volume of ether. The equation for the reaction is $B_4H_{10} + LiCH_3 \rightarrow LiB_4H_9 + CH_4$. While LiB_4H_9 is stable at −78°, it slowly decomposes at temperatures as low as −63°.

Lithium nonahydrotetraborate reacts with gaseous HCl and DCl at −78° to produce B_4H_{10} and B_4H_9D, respectively. The presence of a single deuterium atom in the latter substance was confirmed by mass spectral analysis. Four infrared spectra of B_4H_9D taken over a period of 40 min after its initial generation indicated that deuterium was originally present in a bridge position, but that ultimately intramolecular exchange takes place. This was previously observed by Norman and Schaeffer.[16]

Neither B_2H_6 nor B_5H_9 reacts with LiB_4H_9 in ether at −78°. Decaborane(14) reacts under these conditions to produce B_4H_{10}. The solution at the end of this reaction was an intense lemon-yellow color, characteristic of the $B_{10}H_{13}^-$ anion. Pentaborane(9) was obtained when ether solutions of LiB_5H_8 and B_4H_{10} were brought together. Thus it appears that B_4H_{10} is a

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weaker acid than $B_{10}H_{14}$ but stronger than B_2H_6 and B_5H_9.

Kodama[17] has recently indicated the presence of $B_4H_9^-$ in the diammoniate of pentaborane(11). Johnson and Shore[18] also report that they have prepared salts of $B_4H_9^-$ by a different method.

The details of our work will be described in a later publication.

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* Address correspondence to this author.

A. C. Bond,* M. L. Pinsky
Department of Chemistry, Rutgers, The State University
New Brunswick, New Jersey 08903
Received August 6, 1970

Deprotonation of Tetraborane(10) by Ammonia. The Temperature-Dependent Boron-11 Nuclear Magnetic Resonance Spectrum of $B_4H_9^-$

Sir:

It has been demonstrated that the bridge hydrogens of the intermediate boron hydrides, B_5H_9 and B_6H_{10}, can function as Brønsted acid sites in the presence of strongly basic anions.[1-4] We have recently reported that B_6H_{10} is deprotonated by NH_3,[5] thereby showing that the bridge acidity of this hydride is not restricted to reactions with strongly basic anions. At this time, we wish to report that in the initial reaction of tetraborane(10) with ammonia in ether at low temperature, the boron hydride is deprotonated. This observation is significant in that all previously reported reactions of tetraborane(10) with nucleophiles produced as the only identifiable products fragments which arise from bridge cleavage;[6] furthermore, it is in accord with the earlier suggestion of Parry and Edwards[7] that bridge hydrogens of the lower boron hydrides interact with ammonia.

$$B_4H_{10} + NH_3 \xrightleftharpoons{(C_2H_5)_2O} NH_4^+B_4H_9^- \qquad (1)$$

At −65°, $NH_4^+B_4H_9^-$ was observed exclusively in the initial boron-11 nmr spectrum of the sample. Upon standing, the bridge cleavage product, $BH_2(NH_3)_2^+$-$B_3H_8^-$, and B_4H_{10} appeared simultaneously in the spectrum. As the temperature was raised, reaction 2 accelerated and the $NH_4^+B_4H_9^-$ disappeared as the products of reaction 2 were formed. No H_2 formed.

$$B_4H_{10} + NH_3 \xrightarrow{(C_2H_5)_2O} {}^1\!/_2BH_2(NH_3)_2^+B_3H_8^- + {}^1\!/_2B_4H_{10} \qquad (2)$$

This result suggests the possibility of competing reactions involving ammonia and tetraborane(10): a rapid, reversible reaction in which the ammonium salt is formed through deprotonation of B_4H_{10} (eq 1); and a slower irreversible reaction in which bridge cleavage occurs (eq 2).

The $B_4H_9^-$ anion produced in reaction 1 was identified by its boron-11 nmr spectrum which was identical with that of KB_4H_9 prepared through the reaction of KH with B_4H_{10} in diethyl ether.[8] In addition, $(n\text{-}C_4H_9)_4$-NB_4H_9 was prepared from $NH_4^+B_4H_9^-$ through the following metathesis reaction and identified by boron-11 nmr.

$$NH_4^+B_4H_9^- + (n\text{-}C_4H_9)_4NI \xrightarrow[-78°]{CH_2Cl_2-(C_2H_5)_2O} (n\text{-}C_4H_9)_4NB_4H_9 + NH_4I\downarrow \qquad (3)$$

Also, $(n\text{-}B_4H_9)_4NB_4H_9$ was prepared from KB_4H_9.[10]

$$KB_4H_9 + (n\text{-}C_4H_9)NI \xrightarrow[-35°]{CH_2Cl_2-(C_2H_5)_2O} (n\text{-}C_4H_9)_4NB_4H_9 + KI\downarrow$$

The identity of the NH_4I and the KI produced in these reactions was established by X-ray powder diffraction. The product $BH_2(NH_3)_2^+B_3H_8^-$ from reaction 2 was identified from its boron-11 nmr spectrum and its X-ray powder diffraction pattern. Tetraborane(10) from reaction 2 was identified by its boron-11 nmr spectrum. The area ratios obtained from the boron-11 nmr spectrum and a mass balance of the products recovered from reaction 2 established the stoichiometry. For purposes of the nmr study, $B_4H_9^-$ was generated from the deprotonation of B_4H_{10} by KH in diethyl ether at −78°. Hydrogen evolution was rapid and nearly quantitative. At room temperature the solution deteriorated noticeably in 20–30 min; at −78° solutions appear to be stable indefinitely. The boron-11 nmr spectrum of the anion was studied over the temperature range −80° to ambient.

The low-temperature spectrum (−80 to −45°) may be assigned on the basis of the 2113 structure proposed by Lipscomb for this anion[11] (see Figure 1). Analogous assignments have been made for the boron-11 nmr spectra of the isoelectronic species B_4H_8L (L = CO,[12] PF_3,[12] $PF_2N(CH_3)_2$,[13] and PF_2H[13]); this type of structure for $B_4H_8PF_2N(CH_3)_2$ has been established by X-ray diffraction studies.[14] Thus, at −45° a triplet of relative intensity 1.0 is observed (δ 53.2 ppm relative to $BF_3\cdot O(C_2H_5)_2$, J = 96 Hz), and two broad, unresolved resonances with a total combined relative intensity of 2.8 are also present (δ 9.7 and 0.4 ppm). The triplet may be assigned to B_1, the resonance at 9.7

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