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Alkali Metal Salts Derived from Pentaborane(9) and Hexaborane(10): MB_5H_8 and MB_6H_9[1]

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The alkali metal salts MB_5H_8 and MB_6H_9 have been prepared by the reaction of the parent boron hydrides with $LiCH_3$, NaH, and KH in a variety of ether solvents. Sodium and potassium salts have been isolated as microcrystalline solids of limited thermal stability. The $B_6H_9^-$ ion is more stable than the $B_5H_8^-$ ion with respect to thermal decomposition in solution and in the solid state. Boron-11 nmr spectra of the anions are similar in general appearance, each consisting of two symmetrical doublets. The higher field doublet in each spectrum is assigned to an apical boron and the lower field doublet to magnetically equivalent basal borons in pyramidal structures which are closely related to the parent hydrides. Variable-temperature boron-11 nmr spectra militate against the existence of static geometric isomers over the temperature range studied.

Introduction

Early attempts to effect the reaction of B_5H_9 with NaH in ethyl ether were unsuccessful.[3] However, with LiH in ethyl ether an uncharacterized solid of composition $B_5H_9 \cdot 2LiH$ was reported.[4] Recently Onak, Dunks, Searcy, and Spielman[5] found that both LiH and NaH deprotonate B_5H_9, albeit slowly, in ethyl ether at room temperature, thereby establishing the Brønsted acidity of B_5H_9. Such acidic character for a lower boron hydride was predicted in 1959.[6] The Brønsted acidity of $B_{10}H_{14}$ is well established.[7]

Preliminary reports of the preparation and characterization of the conjugate base of B_5H_9, the octahydropentaborate(−1) ion, $B_5H_8^-$, were published by Gaines and Iorns[8] and Geanangel and Shore.[9] A new class of pentaborane(9) derivatives[10-12] has since been prepared by means of this anion, and an analogous ion, $B_6H_9^-$, has been derived from B_6H_{10}.[13] The reaction of LiB_5H_8 with B_2H_6 is of significant value for the preparation of $B_{10}H_{14}$ and B_6H_{10}.[9]

In the present report, we provide details on the preparation and isolation of the alkali metal salts of $B_5H_8^-$ and $B_6H_9^-$, their stabilities, and variable-temperature boron-11 nmr spectra.

Results and Discussion

Deprotonation Reactions.—Pentaborane(9) and hexaborane(10) are rapidly and quantitatively deprotonated in ether solvents at low temperature (−45 to −80°) through the general reactions

$$B_5H_9 + MB \longrightarrow MB_5H_8 + HB$$
$$B_6H_{10} + MB \longrightarrow MB_6H_9 + HB$$

where MB = $LiCH_3$, NaH, or KH. As a deprotonating agent, NaH is considerably less reactive than KH. Reaction temperatures at least 15–20° higher are necessary to achieve a comparable reaction rate when NaH is used. No reaction occurs in the absence of solvent or with a hydrocarbon solvent. In ether solvents the reaction rate is qualitatively observed to increase with increasing base strength in the order: diethyl ether < glyme (1,2-dimethoxyethane) < dimethyl ether $\sim$ tetrahydrofuran. Neither sodium nor potassium hydride is useful for deprotonating B_5H_9 in diethyl ether although both have been shown to react in the more basic ethers. In all cases, however, B_5H_9 reacts more slowly than B_6H_{10}, which is to be expected from their relative Brønsted acidities.[13]

Physical Properties and Thermal Stability of $B_5H_8^-$ and $B_6H_9^-$ Salts.—Solutions of the alkali metal hydroborate salts MB_6H_9 and MB_5H_8 are clear and colorless and noticeably viscous at concentrations of 1–2 *M* especially for the lithium salts. Slow removal of solvent at low temperature yields well-formed transparent crystals which are solvates. Complete removal of the solvent is not possible for the lithium salts even at room temperature; only very viscous, partly decomposed syrups are obtained. However, it is possible to isolate KB_6H_9 and NaB_6H_9 from dimethyl or diethyl ether and KB_5H_8 from dimethyl ether at −45° without decomposition. These compounds are obtained as very fine white microcrystalline powders of limited thermal stability. If the solvent is replaced immediately, the compounds dissolve completely and their boron-11 nmr spectra are identical with those of freshly prepared solutions. However, the infrared spectrum of solid KB_5H_8 in Nujol shows evidence of decomposition even when first recorded after a period of approximately 1 hr

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[1] Presented in part at the 155th and 157th National Meetings of the American Chemical Society, San Francisco, Calif., April 1968, and Minneapolis, Minn., April 1969.

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[8] D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **89**, 3375 (1967).

[9] R. A. Geanangel and S. G. Shore, *ibid.*, **89**, 6771 (1967).

[10] D. F. Gaines and T. V. Iorns, *ibid.*, **89**, 4249 (1967); **90**, 6617 (1968).

[11] A. B. Burg and H. Heinen, *Inorg. Chem.*, **7**, 1021 (1968).

[12] T. V. Iorns and D. F. Gaines, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., 1969, No. INOR 30.

[13] H. D. Johnson, II, S. G. Shore, N. L. Mock, and J. C. Carter, *J. Am. Chem. Soc.*, **91**, 2131 (1969).

at room temperature. Solid KB_6H_9 is considerably more stable; its infrared spectrum and X-ray powder pattern show that complete decomposition has not occurred even after 1 week at room temperature in a dry nitrogen atmosphere.

Potassium octahydropentaborate(−1), KB_5H_8, and KB_6H_9 are not appreciably soluble in diethyl ether but dissolve in dimethyl ether, glyme (1,2-dimethoxyethane), and tetrahydrofuran. The $B_6H_9^-$ salts are thermally much more stable in solution than the $B_5H_8^-$ salts and the lithium salts of both anions appear to be slightly more stable than the corresponding sodium and potassium salts. The boron-11 nmr spectrum of LiB_5H_8 in ethyl ether is unchanged after 1 hr at room temperature, at which time the solution is slightly turbid. No yellowing of the solution is noticeable at this point. In the presence of unreacted pentaborane(9) the solution becomes yellow and decomposes significantly in this time interval.

The salt KB_5H_8 is much more stable in solution than was previously reported.[9] From its boron-11 nmr spectrum, no sign of decomposition was indicated over a period of several hours at 0° in dimethyl ether or tetrahydrofuran. A fine white precipitate does appear immediately after warming the solution to room temperature; however, only after approximately 1 hr at this temperature is decomposition evident from the boron-11 nmr spectrum. The white precipitate does not redissolve when the temperature of the solution is lowered. It is the result of decomposition of the $B_5H_8^-$ ion. As the decomposition progresses in glyme, the two symmetrical doublets initially present decrease in intensity as peaks at 5.0, 11.8, 19.6, and 27.1 ppm (relative to $BF_3 \cdot O(C_2H_5)_2$ at 19.3 Mhz) appear. From such a system we have been able to isolate $N(CH_3)_4B_5H_8$,[9] a salt in which the $B_5H_8^-$ ion appears to be a structural isomer of the anion discussed in the present paper. Several salts of the isomeric $B_5H_8^-$ ion will be discussed in a later paper.

The Structures of $B_5H_8^-$ and $B_6H_9^-$.—Gaines and Iorns[8] have shown that LiB_5H_8 reacts with HCl or DCl to form B_5H_9 or μ-DB_5H_8 in high yields. On the basis of these reactions it was concluded that the $B_5H_8^-$ ion is generated by removal of a proton from the bridge position. In a similar fashion we have shown that B_6H_{10} and μ-DB_6H_9 are regenerated in high yields in the reaction of KB_6H_9[13] or LiB_6H_9 with HCl and DCl. This is strong evidence that the boron framework in each ion is similar to that of the borane from which it is derived. This is confirmed by the qualitative similarity of the boron-11 nmr spectra of each conjugate acid–base pair. Furthermore, direct evidence for removal of a bridge proton from hexaborane(10) has been obtained from a tracer study.[13]

Nmr Spectra of $B_5H_8^-$ and $B_6H_9^-$.—The boron-11 nmr spectra of $B_5H_8^-$,[9] B_5H_9,[14] $B_6H_9^-$, and B_6H_{10}[15] at ambient temperature are qualitatively similar. In each case two symmetrical doublets are observed indicating that each boron atom is spin coupled to one and only one hydrogen atom; furthermore, the doublet at higher field is of relative intensity 1 and is assignable to the unique boron in an apical environment. The remaining doublet is thus due to boron atoms in basal positions.

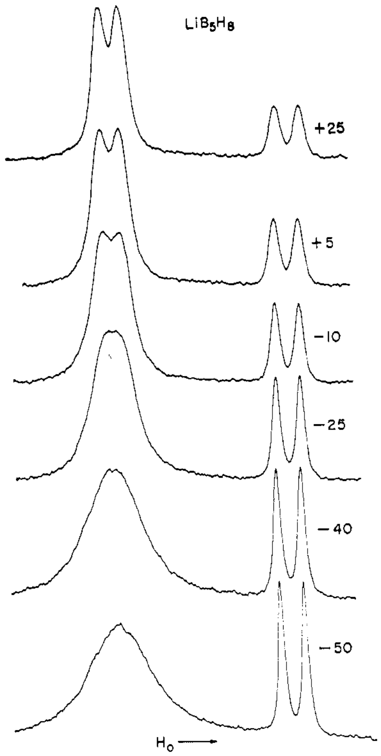

Figure 1.—The 32.1-MHz ^{11}B nmr spectra of LiB_5H_8 in $(C_2H_5)_2O$, 1.5 *M*, at several temperatures.

Figures 1 and 2 depict the variable-temperature boron-11 nmr spectra of LiB_5H_8 and LiB_6H_9, respectively. The spectrum of LiB_5H_8 is simpler than that previously reported.[8,9] It is seen that on cooling, the spectra of the lithium salts change markedly. Much lower temperatures are required to achieve the same effect with the sodium and potassium salts. For example, temperatures of the order of −100° are required to observe spectra of KB_5H_8 solutions which have the appearance of LiB_5H_8 solutions in the −40 to −50° range. The concentration of the anion also affects the appearance of the spectra at low temperature. The lower the concentration of the anion, the lower is the temperature required to observe complete loss of doublet resolution.

These spectral changes are qualitatively related to the observed viscosity of the solutions; at temperatures where severe line broadening is evident, the solutions are too viscous to pour. Under these conditions, extreme line broadening is very probably due to the interaction of boron nuclear quadrupoles ($I = {}^3/_2$) which causes a decrease in the relaxation time.[16] The magni-

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(15) R. E. Williams, S. G. Gibbons, and I. Shapiro, *J. Chem. Phys.*, **30**, 333 (1959); T. P. Onak, H. Landesman, R. W. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(16) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 29.

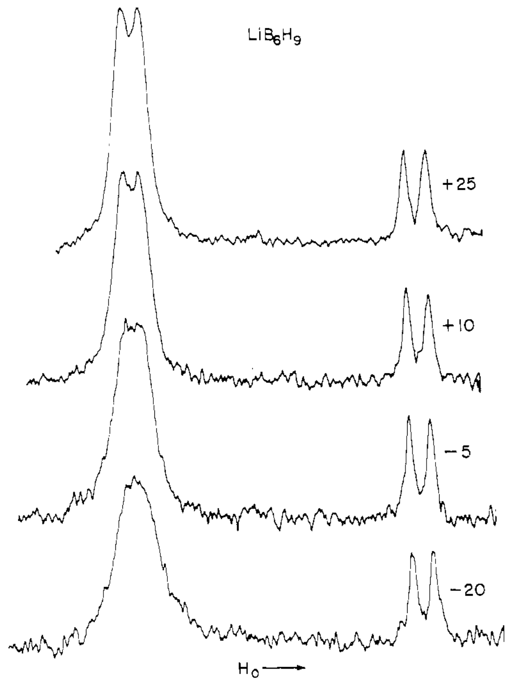

Figure 2.—The 32.1-MHz ^{11}B nmr spectra of LiB_6H_9 in $(C_2H_5)_2O$, 0.7 *M*, at several temperatures.

tude of the broadening is expected to be highly dependent on the local symmetry around the resonating nucleus. The pronounced broadening of the basal doublet with increasing viscosity of the solution is consistent with the asymmetry of the environment of the basal boron atoms in each ion. The fact that the apical doublet is not broadened as the viscosity increases is consistent with high symmetry at the apical site; however, the apical doublet in the spectrum of LiB_5H_8 actually becomes progressively sharper as the solution is cooled. The reason for this behavior is not known.

A sharp singlet is observed in the lithium-7 nmr spectrum of each lithium salt. Neither the line width nor the chemical shift shows temperature dependence in the range −70° to ambient temperature. This suggests that the changes in the boron-11 nmr spectra at low temperature are not caused by direct interaction of the anions with the lithium cation.

In the temperature range studied, the boron-11 nmr spectra of $B_5H_8^-$ and $B_6H_9^-$ militate against the existence of static isomers. The magnetic equivalence of the basal borons in the boron-11 nmr spectra of $B_5H_8^-$ and $B_6H_9^-$ is most likely due to a rapid intramolecular tautomerism. The fact that the basal resonance is of doublet multiplicity is consistent with a mechanism involving the migration of only bridge hydrogens around the base, not terminal hydrogens, and precludes rapid bridge–terminal interchange. The rapid migration of basal terminal hydrogens in $B_5H_8^-$, for example, would give a basal quintet in the absence of rapid bridge–terminal interchange or a basal nonet if rapid bridge–terminal interchange were occurring. The intramolecular mechanism of tautomerism proposed to rationalize the magnetic equivalence of the basal boron atoms in the boron-11 nmr spectrum of B_6H_{10}[17] is applicable to $B_5H_8^-$ and $B_6H_9^-$. This process, illustrated for $B_5H_8^-$ in Figure 3, does not mix terminal and bridge hydrogens because the hydrogens in the BH_2 group in the intermediate are held in the same orientation relative to the apical boron throughout the process.

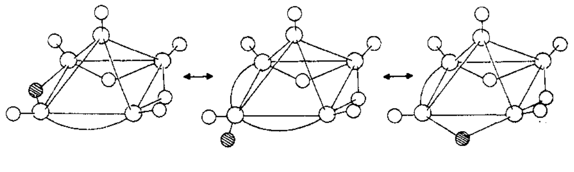

Figure 3.—A mechanism for the tautomerism of the $B_5H_8^-$ ion.

Although a mechanism involving rapid intermolecular exchange of bridge hydrogens is also consistent with the observed nmr spectra, for the following reasons we believe that such exchange does not occur. Exchange of protons between $B_6H_9^-$ and B_6H_{10} does not occur rapidly. This is clearly shown by the boron-11 nmr spectrum of a mixture of LiB_6H_9 and B_6H_{10} in diethyl ether in which both basal doublets are easily identifiable at temperatures below approximately 0°. If exchange of bridge protons were occurring at a rapid rate, only one doublet would be observed at an intermediate chemical shift value. It is even less likely that rapid proton exchange would occur between $B_5H_8^-$ ions or $B_6H_9^-$ ions because this would require the close approach of two negatively charged species which would be energetically less favorable.

Chemical Shifts and Coupling Constants.—The removal of a bridge proton from B_5H_9 or B_6H_{10} should lead to an increase in electron density about the boron atoms in each ion and consequently an increase in the chemical shift value is expected on this basis. In agreement with this expectation, the basal chemical shift for each ion (Table I) is found at higher field than that for the corresponding conjugate acid.

Table I

Boron-11 Nmr Data (32.1 MHz)

	δ(apex)[a]	J_{BH}(apex)	δ(base)[a]	J_{BH}(base)	$\Delta\delta$[b]
B_5H_9	53.1	175	13.6	164	39.5
$B_5H_8^-$	52.8	158	17.0	129	35.8
B_6H_{10}	52.2	158	−13.7	158	65.9
$B_6H_9^-$	50.0	142	−9.0	107	59.0

[a] Relative to $BF_3 \cdot O(C_2H_5)_2$. All values were determined in ether solutions in this laboratory. [b] $\Delta\delta = \delta(\text{apex}) - \delta(\text{base})$.

The fact that the apical resonance in $B_6H_9^-$ is found at significantly lower field than the apical resonance in B_6H_{10} is not consistent with the preceding argument. Rationalization of this downfield shift is possible by considering, in addition to the inductive effect, the effect of changes in diamagnetic circulation using an essentially empirical treatment based on a ring current model which has been developed for pyramidal boron hydrides and carboranes.[18] In this treatment, the

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(17) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 173; R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

pyramidal framework is treated as a cone and the delocalized electrons bonding the apex to the base are distributed in ring current loops on the surface of the curved conical surface. The calculated difference between the apical and basal chemical shifts, $\Delta\delta$, is found to be directly related to the distances of the current loops from the apex and directly related to the radius of the base of the cone while the apical and basal chemical shifts would be inversely related to these parameters. In terms of this model the downfield shift of the apical resonance of $B_6H_9^-$ relative to B_6H_{10} could be due to a shift of the ring current loops toward the base of the cone or to an increase in the radius of the base. It is not reasonable to expect the removal of a bridge proton from the base of the pyramidal structure to result in a shift of the delocalized, framework-bonding electrons toward the base. However, the new basal BB bond could be longer than the previous BHB bond, effectively increasing the radius of the base of the conical model. The downfield chemical shift of the apical resonance of $B_6H_9^-$ may therefore be interpreted as resulting from a decrease in the secondary field created by the "ring current," perhaps partly offset by an increase in electron density. For the apical boron of $B_5H_8^-$, these effects evidently nearly cancel each other. For the basal resonance of each ion the inductive effect dominates; therefore, $\Delta\delta$ is smaller.

Implicit in the preceding discussion is the assumption that changes in temperature-independent paramagnetism are not important in this case. This assumption is considered to be valid only because the structure of each ion is believed to be very similar to that of the borane from which it is derived.

The nonahydrohexaborate(−1) and octahydropentaborate(−1) ions exhibit considerably smaller $^{11}B-^{1}H$ coupling constants than B_6H_{10} and B_5H_9, respectively. This presumably indicates that there is less s character in the terminal BH bonds of the anions and is consistent with preemption of s character by the deprotonated bridge electron pair in the base. Such rehybridization is the rule for more conventional "lone pairs" in a variety of systems.[19]

The reduction of s character in the terminal BH bonds of the anions suggested by the reduction in $^{11}B-^{1}H$ coupling constants connotes a reduction in the terminal BH bond order according to Burg.[11] In agreement with this correlation, the terminal BH stretches in the infrared spectra of KB_5H_8 and KB_6H_9 are found approximately 50 cm^{-1} lower than in B_5H_9 and B_6H_{10}, respectively.

Experimental Section

Materials.—Pentaborane(9) was purchased from Callery Chemical Co. and was used as received. Hexaborane(10) was prepared by the reaction of LiB_5H_8 with B_2H_6.[9] Solutions of $LiCH_3$ in ethyl ether were purchased from Foote Chemical Co. Potassium and sodium hydrides were obtained from Metal Hydrides, Inc. Hydrogen chloride was purchased from the Matheson Co. Deuterium chloride was prepared by treating boron trichloride with D_2O (Mallinckrodt Nuclear Co.) and purified by sublimation from −126° in the vacuum line. Solvents were dried over $LiAlH_4$ and distilled under vacuum into glass storage bulbs with Fisher–Porter Teflon valves.

Apparatus.—Infrared spectra were recorded on a Perkin-Elmer Model 457 infrared spectrometer. Solid samples were run as mulls with Nujol and hexachlorobutadiene between sealed KBr plates. X-Ray powder diffraction patterns were obtained with a Debye–Scherrer camera of 11.46-cm diameter and Cu Kα radiation.

Lithium-7 nmr spectra were obtained at 19.3 MHz at 12,000 G and boron-11 nmr spectra were obtained at 19.3 and 32.1 MHz at 14,000 and 24,000 G, respectively, using Varian high-resolution spectrometers HA-60 and HA-100, respectively, operating in the high-resolution mode. Chemical shifts were measured relative to external standards either contained inside the sample in capillary tubes or by tube interchange. All boron-11 chemical shifts are reported in parts per million relative to $BF_3 \cdot O(C_2H_5)_2$. Samples were prepared in reaction tubes to which 5-mm nmr tubes had been attached by means of a short side arm. The vessel was constructed so that the reaction tube, the nmr tube, and the side arm could be immersed in a dewar flask. Samples were prepared at low temperature in the reaction tube, poured into the nmr tube at low temperature, and frozen at −196°. The nmr tube was then sealed with a torch and removed. In *every* sample preparation, the H_2 or CH_4 evolved was accurately measured in the Toepler system, and samples not evolving more than 95% of the stoichiometric quantity of noncondensable gas were rejected. The reported relative peak areas were determined with a polar planimeter. Care was exercised to record spectra at radiofrequency powers low enough to avoid saturation effects.

Preparation of LiB_5H_8.—In the drybox, 1.00 ml of a 1.50 *M* solution of $LiCH_3$ in diethyl ether was syringed into a reaction tube containing a Teflon-covered magnetic stirring bar. The reaction tube was fitted with a stopcock adapter, placed on the vacuum line, cooled, and evacuated. (When another solvent was desired, the $(C_2H_5)_2O$ was pumped away at this point and an equal volume of the new solvent was added.) With the reaction flask at −196°, 1.50 mmol of B_5H_9 was added and the reaction mixture warmed until the B_5H_9 melted and dissolved (*ca.* −50°). The reaction mixture was stirred at −78° as the extent of reaction was monitored by observing the increase in pressure in the system. The reaction proceeded to completion at −78° in several hours.

Preparation of KB_5H_8 and NaB_5H_8.—A 50-ml round-bottom flask containing a Teflon-covered magnetic stirring bar was flushed with dry nitrogen gas, sealed with a rubber stopper, and accurately weighed on the analytical balance. In the drybox, KH was transferred to this flask which was then restoppered, removed from the drybox, and reweighed. The flask was fitted with a stopcock adapter in the nitrogen atmosphere of a polyethylene glove bag and evacuated on the vacuum line. One milliliter of $(CH_3)_2O$ per millimole of KH and an equimolar amount of B_5H_9 were added at −196°. Reactions of 1–2 mmol were run at −78°, but the reaction was very vigorous; larger scale reactions were initiated at −95°. The preparation of up to 10-mmol quantities of KB_5H_8 in $(CH_3)_2O$ was carried out by adding B_5H_9 and allowing it to react in 3–5-mmol increments.

Solid KB_5H_8 was isolated from $(CH_3)_2O$ by distilling away the bulk of the solvent at −78° and then warming to −45° to pump away the rest.

X-Ray powder diffraction pattern data for KB_5H_8, *d* (relative intensity): 9.5 (s), 5.34 (s), 5.05 (s), 4.77 (m), 3.91 (s), 3.27 (w), 3.12 (s), 2.96 (s), 2.69 (m), 2.53 (m), 2.44 (w), 2.22 (w), 2.16 (w), 2.03 (w), 1.97 (w), 1.89 (w).

Infrared spectrum of KB_5H_8 (cm^{-1}): 2540 (s), 2500 (s), 2470 (s), 1790 (w, b), 1335 (vw), 1275 (vw), 1255 (w), 1085 (vw, b), 1060 (vw, b), 1030 (vw), 990 (m), 920 (w), 890 (w), 860 (vw), 840 (m), 720 (w), 625 (m), 605(m), 540 (m).

A similar procedure was used to prepare NaB_5H_8 from NaH

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(18) T. Onak, D. Marynick, and P. Mattschei, *Chem. Commun.*, 557, 1968; D. Marynick and T. Onak, *Inorg. Chem.*, **7**, 1754 (1968); D. Marynick and T. Onak, *J. Chem. Soc.*, 1742 (1969).

(19) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

and B_5H_9 in tetrahydrofuran. The reaction proceeded to completion at a moderate to slow rate at −63°.

Preparation of LiB_6H_9.—In a typical reaction, 1.00 ml of an ethyl ether solution, 1.5 *M* in $LiCH_3$, was syringed in the drybox into a 20–25-mm diameter reaction tube containing a Teflon-covered stirring bar. The reaction tube was fitted with a stopcock adapter, attached to the vacuum line, cooled, and evacuated. Hexaborane(10) was measured in a calibrated volumetric tube at 0° (0.69 g/ml)[20] and 0.163 ml (1.50 mmol) was distilled into the reaction flask at −196°. The reaction vessel was warmed until the B_6H_{10} melted (near −62°) and dissolved in the ether; then it was thermostated at −78°. The reaction was immediate and vigorous; a quantitative amount of methane was evolved in minutes. Samples no larger than 3 mmol were prepared by the procedure. This reaction was also carried out in methyl ether and glyme by removing ethyl ether from the $LiCH_3$ and replacing it with an equivalent volume of the new solvent.

Preparation of KB_6H_9 and NaB_6H_9.—A quantity of KH or NaH, 1–3 mmol, was accurately weighed in a 20–25-mm diameter reaction tube as previously described in the preparation of KB_5H_8 and NaB_5H_8. An equimolar amount of B_6H_{10} was distilled into the reaction tube and allowed to melt and run to the bottom. One milliliter of solvent per millimole of hydride was then added and the mixture was warmed to an appropriate reaction temperature and stirred. Reaction temperatures suitable for 1–2-mmol preparations are as follows: KH in $(CH_3)_2O$, −78°; KH in THF, −78°; KH in glyme, −50°; KH in $(C_2H_5)_2O$, −50°; NaH in THF, −63°; NaH in glyme, −45°; NaH in $(C_2H_5)_2O$, −45°.

KB_6H_9 and NaB_6H_9 were isolated as white, free-flowing, fine powders from $(CH_3)_2O$ or $(C_2H_5)_2O$ by pumping away the solvent at −45°.

X-Ray powder diffraction pattern data for KB_6H_9, *d* (relative intensity): 8.9 (m), 5.72 (w), 5.11 (vs), 4.42 (m), 3.82 (s, b), 3.36 (vw), 2.95 (m) 2.55 (m), 2.45 (vw), 2.24 (vw), 2.03 (w), 1.93 (w), 1.90 (w).

Infrared spectrum of KB_6H_9 (cm^{-1}): 2540 (s, sh), 2490 (s, b), 1995 (w, b), 1890 (w), 1060 (m), 1005 (m), 820 (m), 795 (m), 763 (m), 726 (m), 682 (w), 618 (m), 575 (m).

KB_6H_9 was analyzed by decomposition in a mixture of concentrated hydrochloric acid and methanol at 100° for approximately 1 day. The per cent boron was determined by titration of the boric acid–mannitol complex according to standard procedures. The hydrogen was measured in the Toepler system. *Anal.* Calcd for KB_6H_9; B, 56.8; H, 8.03. Found: B, 57.4; H, 7.93.

Regeneration of B_6H_{10} from KB_6H_9 and LiB_6H_9.—Excess HCl was added to 0.67 mmol of LiB_6H_9 in $(CH_3)_2O$ at −196°. The mixture was warmed to −78° and stirred for 1 hr. Volatile materials were then slowly passed through traps maintained at −95 and −196°. The reaction flask was not allowed to warm over −45°. In the −95° trap was found 0.62 mmol of B_6H_{10} (93% recovery) identified by mass spectrometry. A similar reaction with 0.68 mmol of KB_6H_9 in $(CH_3)_2O$ yielded 0.56 mmol of B_6H_{10} (82% recovery).

Reactions using DCl were carried out in the same fashion. The mass spectrum of B_6H_9D formed had the peak of maximum intensity in the B_6 mass region at *m/e* 72 (compare B_6H_{10} at *m/e* 71) in agreement with its average composition. The infrared spectrum of B_6H_9D contained an absorption at 1125 cm^{-1} not found in the infrared spectrum of B_6H_{10}. No absorption indicative of terminal deuteration was seen.

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[20] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

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The Thermodynamic Functions of Neptunium(V) and Neptunium(VI)[1]

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The solubility and heat of solution of $NpO_2(NO_3)_2 \cdot 6H_2O$ have been measured, giving values for the free energy and heat of solution of −2940 cal mol^{-1} and 5060 cal mol^{-1}, respectively. Estimation of the entropy of $NpO_2(NO_3)_2 \cdot 6H_2O$ as 123.4 gibbs mol^{-1} then fixes the entropy of $NpO_2^{2+}(aq)$ as -20 ± 2 gibbs mol^{-1}. The heat of reduction of $NpO_2^{2+}(aq)$ to $NpO_2^+(aq)$ by hydrogen peroxide was found to be −10,310 cal mol^{-1} and $E°$ for the NpO_2^{2+}–NpO_2^+ couple was measured as −1.236 V. These data permit calculation of the entropy of $NpO_2^+(aq)$ as -6.2 ± 2 gibbs mol^{-1}. By comparison of the $E°$ for the NpO_2^{2+}–NpO_2^+ electrode and the formal potential reported elsewhere, corrections could be estimated for adjusting the UO_2^{2+}–UO_2^+, PuO_2^{2+}–PuO_2^+, and AmO_2^{2+}–AmO_2^+ formal potentials to true $E°$ values. These were found to be −0.163, −1.013, and −1.70 V, respectively.

Introduction

Although a great deal of thermodynamic data are known for actinide element ions and compounds in solution, very little has been determined under conditions where the corrections to normal standard-state conditions can be made. Consequently only one experimental ionic entropy is available, for UO_2^{2+},[4] and only a few heats of formation have been extrapolated to infinite dilution. The oxygenated actinide cations are of particular interest, not only because of their importance in the chemistry of these elements, but also because of their unique structures. Only a few other

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