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Studies on Boron Hydrides. II.[1] Thermal Decomposition of Some Higher Hydroborates

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Recent reports[3] of the pyrolysis of $B_3H_8^-$ to yield $B_{12}H_{12}^{2-}$ prompt us to report some results with higher hydroborates.

The thermal decompositions listed below were demonstrated. Yields are expressed as weight per cent of starting material recovered as product; if a balanced equation is given, they are calculated in the usual manner. The decomposition of $(C_2H_5)_3NHB_{10}H_{13}$ and of $B_{10}H_{14}^{2-}$ salts also gave rise to small amounts of $B_{12}H_{12}^{2-}$ salts.

	Yield, %
$2(C_2H_5)_3NHB_{10}H_{13} \xrightarrow{80°} [(C_2H_5)_3NH]_2B_{10}H_{10} + B_{10}H_{14} + H_2$	63
$(C_2H_5)_4NB_{10}H_{13} \xrightarrow{165°} [(C_2H_5)_3N]_2B_{12}H_{12}$	20
$[(C_2H_5)_3NH]_2B_{10}H_{14} \xrightarrow{165°} [(C_2H_5)_3NH]_2B_{10}H_{10} + 2H_2$	90
$[(C_6H_5)_3PCH_3]_2B_{10}H_{14} \xrightarrow{165°} [(C_6H_5)_3PCH_3]_2B_{10}H_{10} + 2H_2$	75[4]
$(C_2H_5)_4NB_{10}H_{15} \xrightarrow{165°} [(C_2H_5)_4N]_2B_{12}H_{12}$	18

The mechanisms of these reactions are obscure. The $B_{10}H_{15}^-$ ion[5] very likely loses hydrogen to form $B_{10}H_{13}^-$,[6,7] which subsequently decomposes. This may occur by an autoprotolysis yielding decaborane, hydrogen, and the hypothetical $B_{10}H_{12}^{2-}$, which would be expected to rapidly eliminate hydrogen to form $B_{10}H_{10}^{2-}$. The $B_{12}H_{12}^{2-}$ ion may arise in a number of ways as it is readily formed from many different hydroborates and boranes.[3b] Three possible modes of its formation, no two of which are mutually exclusive, are combination of decaborane with either $B_{10}H_{10}^{3-}$,[8] a known[3] precursor of $B_{12}H_{12}^{2-}$, or alternatively with $B_{10}H_{13}^-$ to form $B_{11}H_{14}^-$. Diborane and $B_{10}H_{13}^-$ react to form $B_{11}H_{14}^-$,[9] which is converted by hydroborate to $B_{12}H_{12}^{2-}$;[1,3b] other boranes and hydroborates would likely be effective as well. The observation[6] that ethylene glycol dimethyl ether solutions of $NaB_{10}H_{13}$ generate $B_{11}H_{14}^-$ on standing at room temperature points to another source of this ion.

We have pyrolyzed $(C_2H_5)_3NHB_{10}H_9D_4$, prepared from 1,2,3,4-$B_{10}H_{10}D_4$,[10] at 80° and examined the deuterium distribution in the resulting $[(C_2H_5)_3NH]_2B_{10}H_6D_4$ by ^{11}B nuclear magnetic resonance spectroscopy. The stereospecificity of the reaction of 1,2,3,4-$B_{10}H_{10}D_4$ with triethylamine[11] was not observed; instead, the deuterium appeared to be statistically distributed between apical and equatorial positions.

Since the ions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ may be regarded as highly resonance-stabilized structures, the above reactions are somewhat reminiscent of aromatization reactions in organic chemistry, the driving force here being the formation of a polyhedral hydroborate ion.

Experimental Section

Starting materials were prepared according to literature methods. All reactions were run in a nitrogen atmosphere using dry solvents. In every case, product identity was established by all of the following methods: infrared[12] and ^{11}B nuclear magnetic resonance spectra[12] and X-ray powder patterns.

Decomposition of Tridecahydrodecaborate(1−) Salts.—A. A suspension of 0.5 g (2.2 mmoles) of $(C_2H_5)_3NHB_{10}H_{13}$[13] in 50 ml of benzene was refluxed and stirred overnight. On cooling, 0.22 g (0.69 mmole), 63%, of $[(C_2H_5)_3NH]_2B_{10}H_{10}$ separated. It was filtered off and recrystallized from acetonitrile–methylene chloride. The X-ray powder pattern showed faint lines due to $[(C_2H_5)_3NH]_2B_{12}H_{12}$.

The above benzene filtrate was evaporated to dryness under reduced pressure to leave a yellow resin from which a small amount of decaborane, identified by its infrared spectrum, sublimed upon heating under vacuum.

B. A mixture of 1.56 g of $(C_2H_5)_4NB_{10}H_{13}$[13] and 50 ml of mesitylene was stirred under reflux overnight. The slurry was cooled to room temperature and filtered. The filter cake was washed with pentane and recrystallized three times from acetonitrile to yield 0.31 g of pure $[(C_2H_5)_4N]_2B_{12}H_{12}$.

Decomposition of Tetradecahydrodecaborate(1−) Salts. A. A mixture of 1.0 g (1.4 mmoles) of $[(C_6H_5)_3PCH_3]_2B_{10}H_{14}$[14] and 100 ml of mesitylene was refluxed and stirred for 24 hr. The solid phase was removed by filtration and recrystallized twice from acetonitrile to afford 0.75 g (1.05 mmoles), 75%, of $[(C_6H_5)_3PCH_3]_2B_{10}H_{10}$. Nuclear magnetic resonance analysis indicated that this product contained about 5% of the $B_{12}H_{12}^{2-}$ salt.

B. The triethylammonium salt of $B_{10}H_{14}^{2-}$ was treated as above for 0.25 hr. Workup and recrystallization from acetonitrile–benzene afforded a 90% yield of the $B_{10}H_{10}^{2-}$ salt. Its X-

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(2) Author to whom correspondence should be directed at U. S. Naval Hospital, Camp Lejeune, N. C.

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ray powder pattern revealed the presence of very small amounts of $[(C_2H_5)_3NH]_2B_{12}H_{12}$.

Decomposition of Tetraethylammonium Pentadecahydrodecaborate(1−).—A slurry of 1.0 g of $(C_2H_5)_4NB_{10}H_{15}$ in 20 ml of mesitylene was refluxed and stirred for 24 hr, then cooled to room temperature. The solid phase was collected on a filter, washed with pentane, and recrystallized three times from acetonitrile to yield 0.18 g of $[(C_2H_5)_4N]_2B_{12}H_{12}$.

The mesitylene filtrate was treated at reflux with 1.0 g of triethylamine for 6 hr in an attempt to convert any decaborane which might have been present in this solution to the insoluble $[(C_2H_5)_3NH]_2B_{10}H_{10}$. However, none was formed.

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The Optical Spectrum of Bismuth(I) in the Molten Aluminum Bromide–Sodium Bromide Eutectic[1a]

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Recently Bi^+ was prepared[2] by reduction of dilute solutions of $BiCl_3$ in the molten $AlCl_3$–NaCl eutectic at 310°. It was shown that the absorption spectrum of this ion is rationalized very well in terms of intraconfigurational $6p^2 \rightarrow 6p^2$ transitions split by a ligand field with a symmetry lower than cubic.[3] Because of the important role of the ligands in determining the details of the spectrum, it is interesting to observe the effects of changing from a chloride to a bromide environment. Accordingly, we prepared Bi^+ by reduction of dilute solutions of $BiBr_3$ in the molten eutectic consisting of 68 mole % $AlBr_3$ and 32 mole % NaBr and determined its absorption spectrum in the visible and near-infrared regions.

The experimental and theoretical procedures parallel the previous work[2,3] almost exactly and will not be repeated here. A small difference between these investigations was in the preparation of the hydrogen halides used for the synthesis of aluminum halides. In the present investigation HBr was prepared by direct reaction between H_2 and Br_2 in the presence of a platinum catalyst at 350°.

Figure 1 provides a comparison between the spectrum of Bi^+ in the $AlBr_3$–NaBr eutectic at 250° (curve A) and that of the same entity in the $AlCl_3$–NaCl eutectic at 310° (curve B). (The latter spectrum is taken from ref 2.) The ligands coordinated to Bi^+ have not been identified for either of these media but almost certainly they are either halide or haloaluminate ions. We favor the latter alternative because we expect the concentration of haloaluminate ions in the AlX_3–NaX eutectic melts (X = Cl or Br) to greatly exceed the concentration of halide ions that are not coordinated to aluminum. Thus, in Figure 1 we presume that curve A is a bromoaluminate complex of Bi^+ while curve B is a chloroaluminate complex. The striking similarity between these spectra is evident.

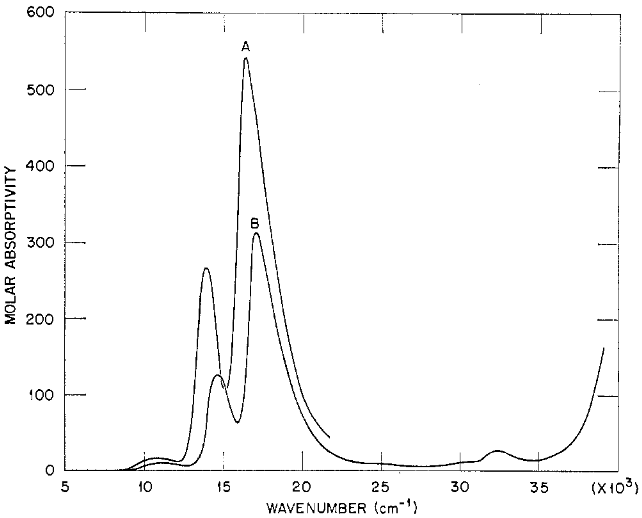

Figure 1.—Spectra of Bi^+ in haloaluminate media. (A) Solvent was molten $AlBr_3$–NaBr eutectic at 250°. (B) Solvent was molten $AlCl_3$–NaCl eutectic at 310° (from ref 2).

Curve A in Figure 1 shows three absorption bands with maxima at about 10,800, 13,900, and 16,400 cm^{-1}. The decidedly skewed shapes of the 10,800 and 16,400 cm^{-1} bands suggest that they consist of two or more unresolved component bands. The 13,900 cm^{-1} band is only slightly skew symmetric but the corresponding band in the chloride melt was unambiguously shown to be a doublet with a separation of about 900 cm^{-1}. We obtained a rough estimate of the splitting of the 10,800 and 13,900 cm^{-1} bands by performing a Gaussian profile analysis with a CDC-1604 computer (see ref 2). The results are listed in Table I.

TABLE I

EXPERIMENTAL AND CALCULATED TRANSITION ENERGIES FOR Bi^+ IN MOLTEN $AlBr_3$–NaBr

Exptl, cm^{-1}	Calcd,[a] cm^{-1}	Excited state[b]
10,300	10,300	$^3P_1$ (±1)
12,100	. . .	
13,700	13,800	$^3P_1$ (0)
14,200	14,200	$^3P_1$ (±2)
16,400	16,100	$^3P_2$ (0)
	16,400	$^3P_2$ (±1)

[a] Parameter values used were $F_2 = 976\ cm^{-1}$, $\lambda = 5020\ cm^{-1}$, $B_0^2 = 8700\ cm^{-1}$, and $B_2^2 = 0$. [b] Notation gives the free-ion origin followed by the J_z value in parentheses.

The secular equation[2] for a p^2 electronic system was fitted to these data with the results shown in Table

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[1] (a) Research sponsored by U. S. Atomic Energy Commission under contract with the Union Carbide Corporation. (b) The Technical University of Denmark, Chemistry Department A, Lyngby, Denmark.

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