Reactions of tetraalkylammonium octahydrotriborates with aluminum tetrahydroborate

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The reactions of $R_4NB_3H_8$ (R = Me, Et, or Bu) with $Al(BH_4)_3$ at 20 °C afforded $R_4N[Al(BH_4)_4]$ and were accompanied by liberation of tetraborane(10) as the major product. The yield of B_4H_{10} increased in going from R = Me to R = Bu.

Key words: octahydrotriborate, aluminum tetrahydroborate, diborane(6), tetraborane(10), pentaborane(9), Lewis acid.

The ability of the $B_3H_8^-$ anion to participate in coordination as a bi- or tridentate ligand[1] and its tendency to undergo decomposition with cleavage of bridging hydrogen bonds and liberation of unstable borane B_2H_4 may be considered as its most typical chemical properties. The $B_3H_8^-$ anion can undergo decomposition upon heating of individual salts MB_3H_8 (M = Na, Mg, Ca, or Sr) *in vacuo*[2—4] as well as in the reactions of octahydrotriborates with Lewis acids and bases,[5—7] after which unstable borane B_2H_4 undergoes dehydrocondensation to form diborane, tetraborane(10), and pentaborane(9). Among the above-mentioned boranes, tetraborane(10) is of particular interest as a convenient reagent in the synthesis of specific polyhedral borane anions. The yield of B_4H_{10} in these reactions depends on the nature of the second component (Lewis acid) and on the temperature.

In this work, we studied the reactions of $R_4NB_3H_8$ (**1**), where R = Me (**1a**), Et (**1b**), or Bu (**1c**), with Lewis acid $Al(BH_4)_3$ (**2**) at 20 °C. The composition and the yields of the resulting gaseous boranes were determined. Previously, the composition of gases evolved in this reaction has not been studied.

Experimental

Compounds **1** were prepared by the exchange reactions of $NaB_3H_8 \cdot 3C_4H_8O_2$ with R_4NBr in water at 20 °C. Octahydrotriborates that formed were recrystallized (**1a** from MeOH, **1b** from EtOH, and **1c** from CH_2Cl_2). Quantitation of H_{hydr} and B demonstrated that the products contained no less than 99% of the major product.

Nonsolvated aluminum tetrahydroborate **2** was synthesized by the reaction of lithium hydroborate with $AlCl_3$. The product was purified by double freezing—thawing in an isolated vacuum system at temperatures from 20 to −78 °C. The vapor pressure of distilled compound **2** was 119.5 Torr at 0 °C, which is consistent with the published data.

The reaction of **1** with **2** was carried out in a 120-mL glass vacuum apparatus equipped with a removable tube. Aluminum hydroborate was condensed into the tube, which contained tetraalkylammonium octahydroborate, cooled to −78 °C. The resulting mixture was warmed to 20 °C over 20—30 min. A powder of compound **1a** was wetted without noticeable dissolution. At the initial stage, compounds **1b** and **1c** were partially dissolved, and then the mixture solidified. At 20 °C and at the ratio **2** : **1** ≤ 1, the gas pressure over the mixture was no higher than 50 Torr, which was substantially lower than the pressure of a vapor of compound **2** (270 Torr at 19 °C). The gas pressure in the system increased with time and reached a constant value after 5—6 h. The gases evolved were passed through three traps cooled to −196 °C, and hydrogen was repeatedly pumped off. Boranes that formed in the reaction were condensed mainly in the first trap. Two other traps were used to prevent breakthrough of boranes and served as reserve vessels. The composition of the boranes that formed was determined according to the following procedure. The trap was warmed from −196 to −125 °C. In this case, only diborane **3** passed into the gaseous phase. The yield of **3** was determined from the vapor pressure in the system. The compound **3** was identified by IR spectroscopy. After removal of compound **3**, the trap was cooled to −196 °C and evacuated with the aim of freeing from a possible admixture of H_2. Then the temperature of the trap was raised to −55 °C to separate tetraborane(10) (**4**) and pentaborane(9) (**5**). In this case, compound **4** passed into the gaseous phase, while compound **5**, if present, should remain in the trap in the solid state. Its amount could be determined from the vapor pressure at 20 °C. The yield of **4** was determined, and **4** was identified analogously to the procedure described for **3** from the vapor pressure in the system and by IR spectroscopy, ν/cm^{-1}: 2610 s, 2590 s, 2580 s, 2500 s, 2300 s, 2160 s, 1400 m, 1280 w, 1180 m, 1150 s, 1080 w, 980 s, 905 w, 860 m, 560 m, 465 m. The solid phase was analyzed for H_{hydr}, boron, and aluminum contents (Table 1).

Results and Discussion

The low gas pressure over the mixture of the initial compounds warmed to 20 °C indicates that the major amount of **2** solidified. Taking into account that the aluminum atom tends to adopt a coordination number of four or even higher, it is evident that the complex salts $R_4N[Al(BH_4)_3B_3H_8]$ were formed at the initial

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Table 1. Composition of the products of the reaction of $R_4NB_3H_8$ (**1a—c**) with $Al(BH_4)_3$ (**2**)

$R_4NB_3H_8$	Initial $R_4NB_3H_8$		Ratio of **1** : **2**	Composition of solid products (%)				Composition of the gas, *m*/mmol (% B)[a]	
	m/g	*N*/mmol	(mol mol^{-1})	H_{hydr}	B	Al	H : B : Al	B_2H_6	B_4H_{10}
1a	1.24	10.82	0.8 : 1	10.10	29.60	13.30	20.3 : 5.5 : 1.0	0.2 (1.2)	2.5 (31)
	1.21	10.55	0.9 : 1	10.10	28.50	14.00	19.3 : 5.1 : 1.0	0.18 (1.1)	2.6 (33)
				[b] 10.05	26.98	16.81	16.0 : 4.0 : 1.0		
1b	0.82	4.80	0.8 : 1	7.30	17.90	11.40	17.1 : 3.9 : 1.0	0.05 (0.7)	1.2 (33)
	0.80	4.69	1.0 : 1	7.30	21.20	11.60	17.1 : 4.5 : 1.0	0.06 (0.8)	1.4 (38)
				[c] 7.45	19.96	12.46	16.0 : 4.0 : 1.0		
1c	1.61	5.7	0.9 : 1	4.90	14.10	7.60	17.3 : 4.6 : 1.0	0.04 (0.5)	1.6 (35)
	1.55	5.5	1.0 : 1	5.00	14.70	8.50	15.5 : 4.3 : 1.0	0.05 (0.6)	1.6 (39)
				[d] 4.90	13.15	8.20	16.0 : 4.0 : 1.0		

[a] Proportion of B with respect to its total content in the initial $R_4NB_3H_8$. [b] Calculated for $Me_4NAl(BH_4)_4$. [c] Calculated for $Et_4NAl(BH_4)_4$. [d] Calculated for $Bu_4NAl(BH_4)_4$.

stage. These compounds were not identified because of their instability. Storage of the complexes *in vacuo* at 20 °C was accompanied by an increase in the pressure in the system due to decomposition of these complexes. The composition of the solid phase that formed has been studied previously and was confirmed in this work.

According to the data of chemical analysis (see Table 1) and IR spectral studies, the solid phase is $R_4N[Al(BH_4)_4]$ (**6**). The IR spectra of compound **6**, except for absorption bands of the cations, are identical, ν/cm^{-1}: 2480 s, 2420 s, 2250 m, 2160 s, 2140 sh, 475 (see Ref. 5).

The general sequence of processes that occurred in the reaction of **2** with **1** can be represented by the following scheme:

$$\underset{\mathbf{1a-c}}{R_4NB_3H_8} + \underset{\mathbf{2}}{Al(BH_4)_3} \longrightarrow R_4N[Al(BH_4)_3B_3H_8] \longrightarrow$$

$$\longrightarrow \underset{\mathbf{6a-c}}{R_4N[Al(BH_4)_4]} + B_2H_4.$$

Unstable B_2H_4 was identified[6] as an adduct with triphenylphosphine $B_2H_4 \cdot 2\ PPh_3$ in the reaction of compound **1c**.

Previously,[7] using the reaction of **1c** with $AlCl_3$ (**7**) as an example, it has been demonstrated that diborane **3** and higher boranes **4** and **5** were formed as a result of dehydrocondensation of B_2H_4. Their yields were 5.3, 25, and 3.7% with respect to the boron content of the initial compound **1c**, respectively. The composition of the gaseous phase obtained in the low-temperature reaction of **1** with **2** under study differs from those obtained in the reactions of pyrolysis of octahydrotriboranes and in the reaction of **1c** with **7** (see Ref. 7). The main difference is that the concentration of tetraborane **4** in the gaseous phase obtained in this work was higher and pentaborane (9) **5** was absent. The formation of **4** from unstable B_2H_4 at 20 °C proceeded, apparently, according to the following scheme:

$$3\ B_2H_4 \longrightarrow B_4H_{10} + 2\ (BH)\ (\text{polymer}).$$

The yield of **4** increased in going from **1a** (32%) to **1c** (39%). A decrease in the reaction temperature by 30 °C compared to that of the reaction with **7** is favorable for retaining compound **4** and increasing its yield by 10—15%. In addition, concentrations of hydrogen and diborane in the gaseous phase decreased (see Table 1). The gas evolved was essentially compound **4** with small admixtures of hydrogen and diborane. The procedure of purification of **4** from **3** and hydrogen presents no problems. The reaction under study can be used for preparing individual tetraborane(10).

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