Alkali Metal Salts

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Facile Synthesis of Unsolvated Alkali Metal Octahydrotriborate Salts MB_3H_8 (M = K, Rb, and Cs), Mechanisms of Formation, and the Crystal Structure of KB_3H_8

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Abstract: *A facile synthesis of heavy alkali metal octahydrotriborates (MB_3H_8; M = K, Rb, and Cs) has been developed. It is simply based on reactions of the pure alkali metals with $THF{\cdot}BH_3$, does not require the use of electron carriers or the addition of other reaction media such as mercury, silica gel, or inert salts as for previous procedures, and delivers the desired products at room temperature in very high yields. However, no reactions were observed when pure Li or Na was used. The reaction mechanisms for the heavy alkali metals were investigated both experimentally and computationally. The low sublimation energies of K, Rb, and Cs were found to be key for initiation of the reactions. The syntheses can be carried out at room temperature because all of the elementary reaction steps have low energy barriers, whereas reactions of $LiBH_4$/$NaBH_4$ with $THF{\cdot}BH_3$ have to be carried out under reflux. The high stability and solubility of KB_3H_8 were examined, and a crystal structure thereof was obtained for the first time.*

The octahydrotriborate anion, $B_3H_8^-$, has attracted widespread attention because its derivatives can be used as chemical hydrogen storage materials ($NH_3B_3H_7$ and $NH_4B_3H_8$),[1–4] chemical vapor deposition (CVD) precursors [$Mg(B_3H_8)_2$ and $Cr(B_3H_8)_2$],[5,6] and reducing agents for a series of organic reactions.[7,8] However, although its synthesis and reactivity have been continually improved and explored, its mechanism of formation has not been fully understood.[8–18] Very recently, our group reported that MB_3H_8 (M = Li and Na) could be synthesized by reacting the corresponding borohydrides with $THF{\cdot}BH_3$ in THF under reflux.[19a] The reaction mechanism of the formation of $B_3H_8^-$ was elucidated, and found to involve a key $B_3H_{10}^-$ intermediate, which undergoes H_2 elimination via a high barrier.[19a] We also found that the nucleophilicity of the B–H bond in BH_4^- and $B_2H_7^-$ played an important role. Surprisingly, this convenient synthetic method did not work for the preparation of KB_3H_8, probably because of the poor solubility of KBH_4 in THF solution.[19]

Herein, we report a facile method for the synthesis of the heavier alkali metal salts of $B_3H_8^-$, MB_3H_8 (M = K, Rb, and Cs), which is based on directly reacting the respective alkali metals with $THF{\cdot}BH_3$ in THF at room temperature. In the current method, no electron carriers, such as naphthalene or triphenylboron, or other reaction media, such as mercury, silica gel, or inert salts, were used, as done in previous works.[8,12–16,20–22] The simplified synthetic method enables the convenient preparation of the heavier MB_3H_8 alkali salts on large scale in very high yields. We also report a detailed study of the mechanism of KB_3H_8 formation and its crystal structure for the first time.

In our new synthetic method, pure alkali metals (M = K, Rb, Cs) are reacted directly with $THF{\cdot}BH_3$ to produce MB_3H_8 and MBH_4 at room temperature according to Equation (1).

$$2\,M + 4\,THF\cdot BH_3 \rightarrow MB_3H_8 + MBH_4 + 4\,THF \quad (M = K, Rb, \text{and } Cs) \tag{1}$$

The reaction rate depended mainly on the particle size of the metals. To prepare KB_3H_8, we cut 5.85 g (150 mmol) of potassium into pieces of approximately $3\times3\times3$ mm^3 in size, and reacted it with 1M $THF{\cdot}BH_3$ solution (300 mL, 300 mmol). The reaction was complete in 12 h, and the reactants were converted quantitatively into KB_3H_8 and KBH_4 according to ^{11}B NMR analysis (see the Supporting Information, Figure S1). Upon completion of the reaction, the KBH_4 precipitate was removed by filtration, and the THF in the filtrate was removed under dynamic vacuum to produce a THF-solvated KB_3H_8 product. Addition of toluene to the THF-solvated product led to the precipitation of unsolvated KB_3H_8, which was isolated in 90% yield upon filtration

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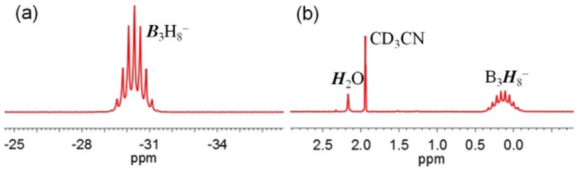

Figure 1. a) ^{11}B NMR and b) ^{1}H NMR spectra of the unsolvated KB_3H_8 in CD_3CN.

(Figures 1 and S2); this represents the highest yield achieved thus far for the preparation of octahydrotriborate alkali metal salts (Table S1).

Similar reactions at room temperature for Rb and Cs produced unsolvated RbB_3H_8 and CsB_3H_8, which were isolated in yields of 70% and 73%, respectively (Figures S3–S10). The reaction times were 5 h for Rb and 2 h for Cs, and thus much shorter than for K. However, similar procedures using Na or Li could not produce NaB_3H_8 or LiB_3H_8 even at elevated temperatures (Figures S11 and S12).

We further investigated the mechanisms of formation of the octahydrotriborate salts from the direct reactions of K, Rb, and Cs with $THF{\cdot}BH_3$ both experimentally and theoretically. Theoretical calculations were performed by density functional theory (DFT) in the Gaussian 09 program.[23] The proposed mechanism includes seven steps (Figure 2 and Figure 3). In the first step, bulk K is solvated by $THF{\cdot}BH_3$ and THF, which is followed by a single-electron donation from the K atom to the BH_3 group in the $THF{\cdot}BH_3$ complex to form BH_3^-. Then, the second K atom donates its valence electron to BH_3^- to form BH_3^{2-}. The free energy barriers of the two transition states (TS) are 4.2 (TS1) and 2.3 kcal mol^{-1} (TS2) for the reactions of K (on the basis of the K gas state) with $THF{\cdot}BH_3$ in THF solvent (Table 1). In the next step, the BH_3^{2-} species undergoes a nucleophilic substitution reaction using its lone pair electrons to replace THF from a second $THF{\cdot}BH_3$ to form $B_2H_6^{2-}$ with an energy barrier of 15.1 kcal mol^{-1} (TS3). This step is exothermic by 71.0 kcal mol^{-1} (Figure 2). Then, $B_2H_6^{2-}$ attacks the B center in a third $THF{\cdot}BH_3$ unit to replace THF using one of its B–H bonds to form $B_3H_9^{2-}$ ($[BH_3BH_2(\mu\text{-}H)BH_3]^{2-}$). The free energy barrier of TS4 was calculated to be 14.4 kcal mol^{-1} in THF solvent (Table 1), which implies that the nucleophilicity of the B–H bond in $B_2H_6^{2-}$ is similar to that of the B–H bond in BH_4^- and $B_2H_7^-$, which reacted with $THF{\cdot}BH_3$ to form $B_2H_7^-$ and $B_3H_{10}^-$ with free energy barriers of 15.8 and 10.3 kcal mol^{-1}, respectively.[19] The nascent $B_3H_9^{2-}$ ion in this reaction is then cleaved to give $B_2H_5^-$ and BH_4^- (TS5) with a free energy of 5.2 kcal mol^{-1} (Figure 3). Finally, the $B_2H_5^-$ intermediate reacts with BH_3 in the fourth $THF{\cdot}BH_3$ adduct to form $B_3H_8^-$ (TS6, 22.3 kcal mol^{-1}), which is converted into the $B_3H_8^-$ final product via TS7 with a free energy barrier of 3.7 kcal mol^{-1}. In another possible pathway, if BH_3^- reacted with two $THF{\cdot}BH_3$ molecules, a $B_3H_9^-$ ($[BH_3BH_2(\mu\text{-}H)BH_3]^-$) ion and not $B_3H_9^{2-}$ would be formed (red part in Scheme S1). This reaction will proceed via two transition

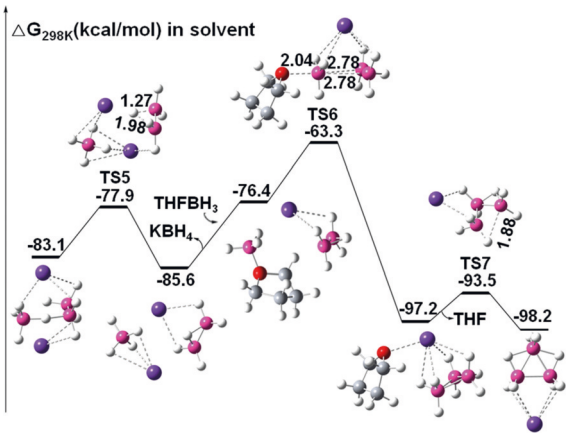

Figure 3. Energy profile for the reaction of $(2K^+)B_3H_9^{2-} \rightarrow KB_3H_8$ calculated at the SMD(THF)/M062X/6–311++G(d,p) level of theory.

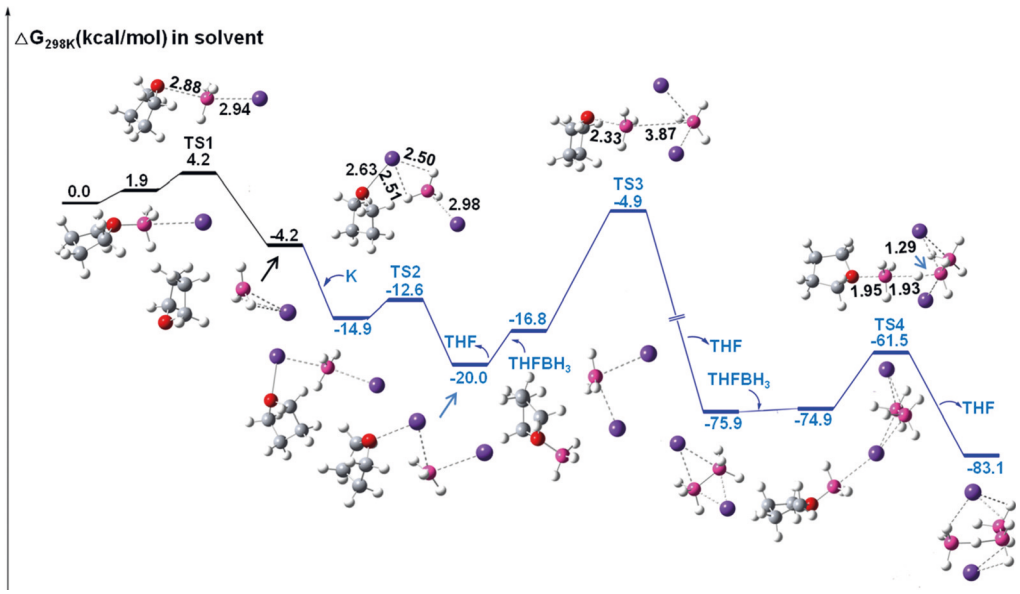

Figure 2. Energy profile for the reaction of $K + THF{\cdot}BH_3 \rightarrow (2K^+)B_3H_9^{2-}$ calculated at the SMD(THF)/M062X/6–311++G(d,p) level of theory.

Table 1: Calculated electronic energies, enthalpies, and free energies.

	ΔE (0 K) [kcal mol^{-1}]	ΔH (298 K) [kcal mol^{-1}]	ΔG (298 K) [kcal mol^{-1}]
($THF{\cdot}BH_3$) (K)	0.0	0.0	0.0
$THF{\cdot}BH_3 + K$	−4.8	−4.0	1.9
TS1	11.7	0.2	4.2
$K^+BH_3^-$-THF	9.7	−5.4	−4.2
($K^+BH_3^-$-THF) + K	−13.9	−27.0	−14.9
TS2	−12.2	−25.7	−12.6
$2\,K^+BH_3^{2-}$-THF	−19.0	−31.7	−20.0
$2\,K^+BH_3^{2-} + THF{\cdot}BH_3$	−34.4	−39.8	−16.8
TS3	−13.1	−25.6	−4.9
$2\,K^+B_2H_6^{2-}$-THF	−79.4	−99.0	−74.1
$2\,K^+B_2H_6^{2-}$	−65.2	−90.6	−75.9
$2\,K^+B_2H_6^{2-} + THF{\cdot}BH_3$	−74.5	−97.0	−74.9
TS4	−65.7	−87.2	−61.5
$2\,K^+B_3H_9^{2-}$-THF	−95.0	−105.5	−81.4
$2\,K^+B_3H_9^{2-}$	−82.6	−97.3	−83.1
TS5	−76.7	−91.0	−77.9
$KBH_4 + KB_2H_5$	−85.4	−98.3	−85.6
$KB_2H_5 + THF{\cdot}BH_3$	−69.3	−89.6	−76.4
TS6	−52.2	−76.8	−63.3
KB_2H_5-BH_3-THF	−90.6	−110.2	−97.2
TS7	−68.7	−96.9	−93.5
KB_3H_8	−91.0	−110.9	−98.2
TS2-1	32.1	9.2	9.3
$K^+B_2H_6^-$-THF	8.1	−6.0	−6.0
TS3-1	23.5	10.8	13.5
$K^+B_3H_9^-$-THF	8.5	−0.2	1.2

states TS2-1 and TS3-1 with relative free energies of 13.5 and 19.5 kcal mol^{-1}, which are much higher than TS2 and TS3 (Table 1). Hence, the reaction via the BH_3^{2-} intermediate is more favorable than the direct conversion of BH_3^- into $B_3H_9^-$.

The proposed mechanism is supported by experimental observations. The reactions of K, Rb, and Cs with $THF{\cdot}BH_3$ can be carried out at room temperature while the reactions of Li and Na borohydrides with $THF{\cdot}BH_3$ have to be run at reflux in THF solution.[19] The different temperature dependence of the two types of reactions is consistent with the different reaction mechanisms. In the reaction of K with $THF{\cdot}BH_3$, the $B_3H_9^{2-}$ intermediate (after TS4 in Figure 3) can be directly cleaved to $B_2H_5^-$ and BH_4^-. The $B_2H_5^-$ intermediate then reacts directly with $THF{\cdot}BH_3$ to form the final $B_3H_8^-$ product. Over all steps, the highest energy barrier is 22.3 kcal mol^{-1} (TS6). Thus the reaction can be carried out at room temperature, but not at low temperatures (Figure S13). The total reaction is exothermic by 98.2 kcal mol^{-1}, and is thus irreversible. On the other hand, in the reaction of $LiBH_4$ with $THF{\cdot}BH_3$ as reported recently,[19] a $B_3H_{10}^-$ intermediate was suggested to be cleaved to B_2H_6 and BH_4^- first; then, dihydrogen interactions between a partially negatively charged $H^{\delta-}$ in the BH_4^- group and the partially positively charged bridging $H^{\delta+}$ in the B_2H_6 molecule lead to the formation of $B_2H_5^-$ and $(H_2)BH_3$. Subsequently, one H_2 molecule is eliminated from $(H_2)BH_3$, and the resulting BH_3 group is combined with $B_2H_5^-$ to form the final $B_3H_8^-$ product. A high energy barrier (31.0 kcal mol^{-1})[19] was found in the dihydrogen interaction, so that this reaction can only take place under reflux with the release of H_2.

The formation of the BH_3^{2-} and $B_2H_6^{2-}$ intermediates was previously monitored by ^{11}B NMR spectroscopy in the reaction of potassium naphthalide and B_2H_6 in THF solution.[24] However, when we monitored the reaction of K with $THF{\cdot}BH_3$ by ^{11}B NMR spectroscopy in the current study, we only observed the starting material $THF{\cdot}BH_3$ and the product KB_3H_8 (Figure S14). The other KBH_4 product is completely insoluble in THF, so that its NMR resonance was not detected but its formation was confirmed by X-ray diffraction (XDR; Figure S15). No intermediate signals were detected in the whole reaction. These observations suggested that the transformation from K(s) to solvated $[K(THF)_6]^+$, and at the same time, from $THF{\cdot}BH_3$ to BH_3^- and BH_3^{2-}, is the rate-determining step, which is consistent with the theoretical results. Under the current conditions, $THF{\cdot}BH_3$ is always present in excess, so that once BH_3^- and BH_3^{2-} have been formed they will be rapidly transformed into the next intermediate all the way to the final product because the energy barriers of all steps are low.

In the current mechanism, the influence of the different alkali metals on the reaction should mainly concern the first two steps, in which the alkali metals donate their valence electron to the BH_3 group to form BH_3^{2-} (black part in Figure 2 and Scheme S1) while the energy profiles in the subsequent steps should be similar for the different alkali metals (blue part and black part in Figure 2, Figure 3, and Scheme S1). Thus we expected the different chemical activities of the alkali metals to be crucial to explain why pure Li and Na could not initiate the reaction. However, the computational results indicated that the free energy barriers of TS1 and TS2 for Li, Na, and K are similar (Table S2). It should be pointed out that the DFT calculations started from the gaseous alkali metal atoms, that is, an M(g) atom reacting with $THF{\cdot}BH_3$ to form BH_3^-, whereas in the experiment, the reaction started from solid metal. Thus, the sublimation energy of the alkali metals must be the key factor that determines whether the reaction proceeds or not. The high sublimation energies of Li (38.0 kcal mol^{-1}) and Na (25.6 kcal mol^{-1}; Table S3)[25] prevent the Li or Na atoms from escaping from the metal lattice to take part in the reaction. This conclusion is supported by the fact that Li/Hg and Na/Hg alloys can react with $THF{\cdot}BH_3$ to form $B_3H_8^-$.[12,22]

Further evidence is provided by the fact that the reaction rate of K with $THF{\cdot}BH_3$ is influenced by the size of the metal species. When potassium metal was cut to $5\times5\times5$ mm^3, the reaction time increased to 20 h, which is significantly longer than 12 h for a smaller piece of potassium ($3\times3\times3$ mm^3), at room temperature. For a smaller particle with a larger surface area, the interaction of K with $THF{\cdot}BH_3$ is enhanced, leading to the faster reaction. Both Rb and Cs have lower melting points than K. Under vigorous stirring, the metal pieces easily deform and seem to display fluid-like behavior. Thus the reactions of Rb and Cs with $THF{\cdot}BH_3$ are much more vigorous, and the reaction times are much shorter.

In the literature, pure alkali metals have been reported to react with $THF{\cdot}BH_3$ to afford MB_3H_8 and MBH_4 (M = Na, K) in moderate yields only when they were adsorbed on silica gel at 160 °C, finely dispersed in inert salts by ball milling,[13,14] or present in the form of a liquid K/Na alloy.[15] Compared with

these previous methods, the current synthetic strategy using pure potassium metal with $THF{\cdot}BH_3$ has several advantages. First, the reaction is carried out without using mercury or any other electron carriers, greatly simplifying the subsequent workup. Furthermore, the quantitative conversion and short reaction time make the reaction much more efficient. Finally, the solubility difference between KB_3H_8 and KBH_4 allows these two compounds to be readily separated: KB_3H_8 is soluble in THF while KBH_4 is almost insoluble in THF.

Unsolvated KB_3H_8 is more stable than unsolvated NaB_3H_8 in the solid state and in aqueous or THF solution (Figure S16).[26] Although NaB_3H_8 is soluble in ethers,[12–14] strong solvation makes it difficult to be accurately weighed for further use.[2,27] Unsolvated NaB_3H_8 can be obtained by dissolving the oily THF-solvated product in diethyl ether and dichloromethane, which will help to break the coordination between THF and the Na^+ cations to completely remove THF.[12–14] For KB_3H_8, the coordination bond between the THF molecule and the potassium cation is so weak that unsolvated KB_3H_8 can be conveniently prepared. After the reaction of potassium and $THF{\cdot}BH_3$ [Eq. (1)], the KBH_4 precipitate was removed by filtration, and the THF in the filtrate was removed under dynamic vacuum to produce THF-solvated KB_3H_8 product. The addition of toluene to the THF-solvated product led to the precipitation of unsolvated KB_3H_8. With pure unsolvated KB_3H_8 in hand, its structure was characterized by synchrotron X-ray powder diffraction (XRPD; see Figure S17 for the refinement profile). Most of the diffraction peaks can be indexed into a monoclinic unit cell in space group $P2_1$ (No. 4), with lattice parameters of $a =$ 5.4804 Å, $b = 8.2153$ Å, $c = 5.4926$ Å, and $\beta = 95.271°$. Details of the structure solution can be found in the Supporting Information (Tables S4 and S5). Figure 4 shows bridging K–H bonds in the range of 2.849 to 3.112 Å. Each K cation coordinates to six B_3H_8 anions with an overall K/B_3H_8 ratio of 1:1. There are two types of asymmetric K–H bridges linked through each pair of K cation and $B_3H_8^-$ anion to construct the 3D molecular structure. The obtained K–B distances are in the range of 3.175 to 3.457 Å, and slightly longer than the Na–B distances of 3.130–3.370 Å in the analogous structure of NaB_3H_8.[12]

In summary, we have shown that unsolvated MB_3H_8 (M = K, Rb, and Cs) can be conveniently prepared by reactions of pure alkali metals with $THF{\cdot}BH_3$ in THF in very high yield at room temperature without using toxic diborane, electron carriers, or other reaction media, such as mercury, silica gel, or inert salts. The structure of unsolvated KB_3H_8 was further determined by synchrotron X-ray powder diffraction. The mechanisms of the reactions were investigated both experimentally and theoretically. The relatively low energy barriers of all elementary steps in the proposed mechanism are consistent with the fact that the reaction can be carried out at room temperature, which is different from the reaction of $LiBH_4/NaBH_4$ with $THF{\cdot}BH_3$ under reflux. The physical properties of the alkali metals control the reactions. The high sublimation energies of Li and Na prevent them from reacting with $THF{\cdot}BH_3$ to produce Li/NaB_3H_8. The low melting points of Rb and Cs lead to more vigorous reactions and higher reaction rates.

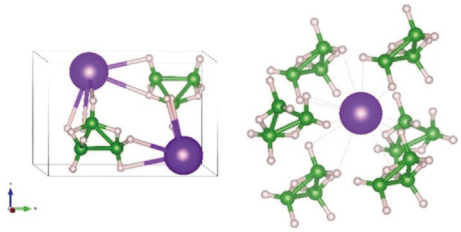

Figure 4. Crystal structure of KB_3H_8 in a unit cell (left) and local coordination of a K cation with six $B_3H_8^-$ anions (right). B green, H pink, K purple.

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Conflict of interest

The authors declare no conflict of interest.

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