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FINAL REPORT,
INVESTIGATION OF LIQUID-METAL HYDRIDES

L. R. Grant
F. C. Gunderloy, Jr.
R. I. Wagner
E. F. Witucki

Rocketdyne, A Division of North American Aviation, Inc.
6633 Canoga Avenue, Canoga Park, California

TECHNICAL REPORT AFRPL-TR-67-134

April 1967

In addition to security requirements which must be met, this document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL (RPR-STAINFO), Edwards, California 93523.
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FOREWORD

This final report is submitted in compliance with Contract AF04(611)-11532, Part I, Paragraph B.1, Line Items 6 and 7. This research program was sponsored by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards Air Force Base, California. Messrs. G. A. Beale and R. A. Biggers of RPCL served as project monitors.

The program was conducted in the Chemical and Materials Sciences Department (Manager, Dr. J. Silverman), Rocketdyne Research Division. Drs. J. Silverman and Emil A. Lawton (Manager, Synthetic and Propellant Chemistry) served as Program Managers. Personnel contributing to the program were:

Dr. Louis R. Grant (Responsible Scientist)
Dr. Frank C. Gunderloy, Jr. (part-time)
Dr. Ross I. Wagner
Mr. Edward F. Witucki (part-time)

This report has been assigned the Rocketdyne report number R-7002.

This technical report has been reviewed and is approved.

W. H. EBELKE, Colonel, USAF
Chief, Propellant Division
Studies of liquid beryllium hydride synthesis have resulted in a number of new species with theoretical specific impulses approaching 330 seconds and further defined the most promising classes of this type of high-energy fuel. In general, it appears that terminators derived from higher borane fragments (e.g., $\text{BH}_2$) are more advantageous than simple $\text{BH}_3$ terminators. Liquids with $\text{B}_3\text{H}_7$ terminators exhibit high theoretical impulse and satisfactory fluidity, and unlike many $\text{BH}_3$-terminated liquids, are not subject to reversible dissociation.

The bulk of this investigation was concerned with the preparation of borane-terminated beryllium hydride (BTBH) liquids from the reaction of $\text{B}_4\text{H}_{10}$ with beryllium alkyls and alkylberyllium hydrides. The nature of the reaction products was dependent upon the experimental conditions. The use of a $\text{B}_4\text{H}_{10}/\text{Be(\text{CH}_3)_2}$ mole ratio of 0.5 and an extended reaction time yielded the best product, a liquid analyzing as $\text{B}_3\text{H}_7(\text{CH}_3\text{BeH})_2\text{BeH}_2\text{BH}_3$ (specific impulse, 329 seconds with $\text{H}_2\text{O}_2$).

The use of $\text{B}_2\text{H}_6/\text{B}_4\text{H}_{10}$ mixtures simplified the complex reactions involving pure $\text{B}_4\text{H}_{10}$ and solid beryllium compounds. Such mixtures increased the liquefaction rates of the beryllium compounds and also resulted in a significant decrease in the amount of $\text{B}_4\text{H}_{10}$ decomposition during its reactions.

Ethyl-substituted BTBH liquids were synthesized. The compound $\text{B}_3\text{H}_7(\text{C}_2\text{H}_5\text{BeH})_2\text{BeH}_2\text{BH}_3$ (specific impulse, 326 seconds) remained fluid at $-40$ C.

Conditions for the quantitative reaction of $\text{Al(\text{CH}_3)_3}$ and BeMe were established for the preparation of alane-terminated beryllium hydride (ATEH) liquids. The displacement of the alane terminators from ATEH liquids by $\text{B}_2\text{H}_6$, $\text{B}_4\text{H}_{10}$, or $\text{Be(\text{BH}_4)_2}$ demonstrated the feasibility of employing ATEH materials as precursors for BTBH liquids.
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Introduction

The investigation of liquid-metal hydrides is the unclassified title of work performed at Rocketdyne on the preparation of a new class of storable liquid propellants containing beryllium and hydrogen. Because beryllium hydride is the best of the solid or hybrid propellant fuels in terms of theoretical specific impulse, particularly if calculations are carried out with $\text{H}_2\text{O}_2$ as the oxidizer, a great deal of interest has been generated in attempting to develop related storable liquid propellant systems.

The new class of fuels under investigation at Rocketdyne utilizes the ability of borane and alane moieties to terminate polymeric beryllium materials, and as a consequence yield liquid beryllium complexes. For this reason, these materials are referred to as borane- and alane-terminated beryllium hydride fuels.

The previous research effort, conducted under Contract AF04(611)-8550, demonstrated the feasibility of synthesizing borane-terminated beryllium hydride (BTBH) liquid fuels from reactions of known beryllium compounds and boron hydrides and/or their derivatives (Ref. 1). The primary goals of the present program were to prepare new and/or improved borane- and alane-terminated beryllium hydride liquid fuels with good liquid properties, thermal stability, and theoretical specific impulse. Because of the demonstrated greater thermal stability of the first triborane-terminated materials (Ref. 2) and their generally good liquid viscosities, much of the effort reported herein was concerned with the reactions of $\text{B}_4\text{H}_{10}$, a source of triborane groups, and polymeric beryllium compounds. As a consequence of these studies, a number of new BTBH liquids, having calculated specific impulse values approaching 330 seconds, were prepared. The best of these, in terms of specific impulse, was a compound analyzing as $\text{B}_3\text{H}_7$ - $(\text{CH}_2\text{BeH})_2\text{BeH}_2\text{H}_3$ (specific impulse, 329 seconds).

The reaction studies have also provided further definition of both the structural features and the chemical routes that must be pursued in the future development of liquid beryllium hydride. In general, it appears that the use of higher borane terminators, such as $\text{B}_3\text{H}_7$, leads to good...
fluidity and high specific impulse, but that further increases in BeH₂ content must be achieved in a controllable fashion to greatly exceed the 330-second specific impulse level.

(U) The synthetic experimental effort of this program was divided informally into three phases: Phase I, Preparation and Modification Studies; Phase II, Preliminary Characterization of Liquid Products; and Phase III, Tailoring of BTM Fuels. Because of the interrelationship of the work performed under these phases, the results are reported in a combined fashion.
(C) The theoretical specific impulse values of some postulated liquid beryllium fuels are compared with that of BeH₂ in Table 1, and those of actual liquids prepared under this contract are presented in Table 2. The heats of formation presented for the compounds in Tables 1 and 2 were derived from bond energies calculated from the experimental heats of formation of beryllium hydride (Ref. 3), beryllium borohydride (Ref. 4), and beryllium alkyls (Ref. 5). All other bond energy values were excerpted from Ref. 6.

(C) In Table 2, both ethyl- and methyl-substituted BTH liquids are listed, and both borane (BH₃) and triborane (B₃H₇) terminators or their alkyl derivatives are presented. Based on the data presented in Tables 1 and 2, the following facts are noteworthy:

1. Large changes in heats of formation do not appreciably affect performance unless the compound in question contains very few alkyl groups.

2. Alkyl substitution on the boron terminator is more detrimental to the performance than alkyl substitution on the beryllium.

3. Although the relative amount of hydrogen per unit weight is greater in the BH₃ group than in the B₃H₇ moiety, liquids can still be prepared having a calculated specific impulse closely approaching 330 seconds.

4. One ethyl group is better for performance than two methyl groups.
TABLE 1

THEORETICAL PERFORMANCE OF SOME POSTULATED BERYLLIUM COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Estimated Heat of Formation, kcal/mole</th>
<th>Specific Impulse with H₂O₂ (shifting, 1000 - 14.7 psia), seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BeH₂)ₙ</td>
<td>-5.6</td>
<td>357</td>
</tr>
<tr>
<td>H₃B(CH₃BeH)(BeH₂)₉BH₃</td>
<td>-82</td>
<td>352</td>
</tr>
<tr>
<td>H₃B(CH₃BeH)(BeH₂)₆BH₃</td>
<td>-45 (-11)</td>
<td>342 (351)</td>
</tr>
<tr>
<td>H₃B(BeH₂)₂(CH₃BeH)₂BH₃</td>
<td>-47 (-12)</td>
<td>338 (341)</td>
</tr>
<tr>
<td>(CH₃BH₂)₂(BeH₂)₄</td>
<td>-70 (-37)</td>
<td>333 (336)</td>
</tr>
<tr>
<td>H₃B(C₂H₅BeH)₃(BeH₂)₆BH₃</td>
<td>-85</td>
<td>333</td>
</tr>
</tbody>
</table>
# Table 2

## Theoretical Performance of Some Known Beryllium Liquids

<table>
<thead>
<tr>
<th>Compound</th>
<th>Estimated Heat of Formation, kcal/mole</th>
<th>Specific Impulse With $H_2O_2$ (shifting 1000 - 14.7 psia), seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_3H_7(CH_3BeH)_2(BeH_2)BH_3$</td>
<td>-20</td>
<td>329</td>
</tr>
<tr>
<td>$B_3H_7(CH_3BeH)_3(BeH_2)BH_3$</td>
<td>-50</td>
<td>326</td>
</tr>
<tr>
<td>$B_3H_7(C_2H_5BeH)(BeH_2)BH_3$</td>
<td>-10</td>
<td>326</td>
</tr>
<tr>
<td>$B_3H_7(CH_3BeH)_2BH_3$</td>
<td>-15</td>
<td>320</td>
</tr>
<tr>
<td>$C_2H_2BH_2(C_2H_5BeH)(BeH_2)BH_3$</td>
<td>-20</td>
<td>311</td>
</tr>
<tr>
<td>$(B_3H_7)_2(C_2H_5BeH)_4(BeH_2)$</td>
<td>-20</td>
<td>315</td>
</tr>
<tr>
<td>$(B_3H_7)_2(C_2H_5BeH)_3(BeH_2)$</td>
<td>-10</td>
<td>317</td>
</tr>
<tr>
<td>$(CH_3B_3H_6)_2(CH_3BeH)_3(BeH_2)$</td>
<td>-35</td>
<td>321</td>
</tr>
</tbody>
</table>
DISCUSSION AND RESULTS

PREPARATION OF THE BTBH LIQUIDS

Reactions involving the agents shown in Table 3 have been used to convert known beryllium-containing solids to BTBH liquids.

TABLE 3

COMPONENTS OF BTBH LIQUIDS

<table>
<thead>
<tr>
<th>Beryllium Compounds</th>
<th>Borane Agents</th>
<th>Beryllium-Boron Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>([(\text{C}_2\text{H}_5)_2\text{Be}]_n)</td>
<td>(\text{B}<em>4\text{H}</em>{10})</td>
<td>(\text{Be}(\text{BH}_4)_2)</td>
</tr>
<tr>
<td>([(\text{C}_2\text{H}_5)_2\text{Be}]_n)</td>
<td>(\text{B}_2\text{H}_6)</td>
<td>((\text{CH}_3\text{BeBH}_4)_2)</td>
</tr>
<tr>
<td>([(\text{C}_2\text{H}_5)_2\text{Be}^{\cdot}\text{C}_2\text{H}_5\text{BeH}]_n)</td>
<td>alkylidiboranes</td>
<td></td>
</tr>
<tr>
<td>([\text{CH}_3\text{BeH}]_n)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{BeH}_2)_n)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These reactions are quite complex, in most instances, and involve several steps (not necessarily in the sequence presented):

1. Direct termination of a polymeric beryllium compound with a borane agent, or a beryllium–boron agent.
2. Chain scission of the polymeric beryllium compound followed by termination with a borane moiety.
3. Hydriding of the beryllium–alkyl bond by the borane agent with the concomitant formation of a boron–alkyl species.

The simplest of the BTBH liquids to prepare are those involving dimethylberyllium and \(\text{Be}(\text{BH}_4)_2\) or \((\text{CH}_3\text{BeBH}_4)_2\). However, the calculated specific impulse (310 to 315 seconds) of these materials indicated they were

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unsatisfactory propellants. The thermal stability of a few BH$_3$-terminated liquids have been examined (Ref. 2), although no systematic investigation was conducted. The liquids studied were chosen on the basis of availability and were tested for their stability as media for (BeH$_2$)$_x$ gels. In all cases, some gas was evolved at 160 F which proved to be primarily B(CH$_3$)$_3$. This borane derivative cannot serve as a terminator and, consequently, when it is formed as a result of internal rearrangement, it is readily evolved. The compound (CH$_3$B$_3$H$_6$)$_2$(CH$_3$BeH)$_3$BeH$_2$, however, was much more stable, even though a B-CH$_3$ bond was already present in the material. On this basis, B$_3$H$_7$ termination appeared to be a logical approach to the preparation of thermally stable BTBH liquids.

(U) A summary of the B$_4$H$_{10}$ reactions investigated is presented in Table 4. A more detailed description of the reactions is presented in the following paragraphs.

B$_4$H$_{10}$/Be(CH$_3$)$_2$ Reaction System

(C) The reaction of B$_4$H$_{10}$ and Be(CH$_3$)$_2$ was found to yield liquids of high theoretical specific impulse (Table 2). However, the composition of the products was dependent, to a large degree, upon the experimental conditions used (Table 4). The following variables were investigated in an attempt to establish those conditions best suited for the preparation of a BTBH liquid with a calculated specific impulse $\approx 2350$ seconds.

1. Relationship of the physical state of B$_4$H$_{10}$ to its reactivity
2. Mole ratios of the reactants
3. Reaction time
4. Effect of B$_2$H$_6$ as an initiating agent for Be(CH$_3$)$_2$ liquefaction

Throughout those studies, temperatures were maintained at ambient or below to hold the decomposition of B$_4$H$_{10}$ (one of the unstable boranes) to a minimum. However, such decomposition was not completely avoidable.
### Table 4

**Summary of $\text{B}_4\text{H}_{10}/\text{Be(CH}_3)_2$ Reactions**

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>$\text{B}<em>4\text{H}</em>{10}/\text{Be(CH}_3)_2$ Mole Ratio</th>
<th>Reaction Conditions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>Liquid $\text{B}<em>4\text{H}</em>{10}$ at ambient temperature</td>
<td>No significant amounts of liquid beryllium products were formed. The principal beryllium-containing product was $\text{BeH}_2$.</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>$\text{B}<em>4\text{H}</em>{10}$ vapor at ambient temperature</td>
<td>Liquefaction of the $\text{Be(CH}_3)_2$ occurred after 26 hours. The liquid analyzed as $\text{[(CH}_3)_2\text{B}<em>4\text{H}</em>{10}]_2(\text{BeH}_2)_2(\text{CH}_3\text{BeH})_2$.</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>$\text{B}<em>4\text{H}</em>{10}$ vapor at ambient temperature</td>
<td>The beryllium alkyl was converted to liquid products in less than 20 hours. After 23 hours, solids precipitated from the reaction mixture, and continued to do so until the reaction was stopped after 29 hours. Analyses of this solid product were not performed.</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>$\text{B}<em>4\text{H}</em>{10}$ vapor at ambient temperature</td>
<td>Formation of liquid products required 25 hours. Further reaction caused complete solidification of the liquid product after a total reaction time of 97 hours. The product was not analyzed.</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>$\text{B}<em>4\text{H}</em>{10}$ added incrementally at ambient temperature</td>
<td>Conversion of the $\text{Be(CH}_3)_2$ to liquid products was complete after 120 hours. A liquid analyzing as $\text{B}_7\text{H}_7(\text{CH}_3\text{BeH})_2\text{BeH}_2\text{BeH}_2$ was isolated.</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>$\text{B}<em>4\text{H}</em>{10}$ added incrementally at ambient temperature</td>
<td>After 120 hours, a liquid was isolated which analyzed as $\text{B}_7\text{H}_7(\text{CH}_3\text{BeH})_2\text{BeH}_2\text{CH}_3$.</td>
</tr>
</tbody>
</table>
(C) Physical State of B₄H₁₀ and Its Reactivity. The products of the \( \text{Be(CH}_3\text{)}_2/B_4\text{H}_10 \) reaction are quite dependent upon the physical state of the B₄H₁₀. The reaction of equimolar amounts of Be(CH₃)₂ and liquid B₄H₁₀, a condition under which hydriding of the beryllium alkyl was expected to be extensive, never yielded a one-phase system. Instead, the slurry of Be(CH₃)₂ and liquid B₄H₁₀ remained colorless, thickened to a maximum after 6 hours, and subsequently became more fluid than the initial mixture before quenching after 29.5 hours. The solid present at the end of this time was the principal beryllium-containing product and was identified as impure BeH₂.

(C) The reaction of equimolar amounts of Be(CH₃)₂ and B₄H₁₀ vapor, however, caused complete liquefaction of the beryllium alkyl after approximately 26 hours. The liquid product, the composition of which corresponded to the empirical formula \( [(\text{CH}_3)_3\text{B.H}_2]_2 (\text{CH}_3\text{BeH})_2(\text{BeH}_2)_2 \), was a mobile liquid, but its high methyl group content negated its importance as a high-energy fuel.

(C) In the presence of liquid B₄H₁₀, the hydriding of Be(CH₃)₂ to BeH₂ is quite rapid. The failure to obtain appreciable quantities of BTHH liquids when liquid B₄H₁₀ was used as the reactant was attributed to the more favorable formation of solid BeH₂ in this reaction medium. Under comparable experimental conditions, however, the B₄H₁₀ vapor-phase reaction, being a solid/gas reaction, was a much slower reaction and the extent of hydriding of the Be(CH₃)₂ was much less. This reasoning is supported by the nature of the products obtained.

(C) Mole Ratios of B₄H₁₀ and Be(CH₃)₂. Although low B₄H₁₀/Be(CH₃)₂ mole ratios would be expected to yield liquids with the higher degrees of polymerization, these conditions would also most likely result in slower Be(CH₃)₂ liquefaction rates, and less hydriding of the beryllium alkyl. Therefore, it was desirable to determine if by altering the mole ratios of the reactants, a compromise could be reached between reaction rates, hydriding, and apparent degrees of polymerization of the final liquid product.
C) Experiments were conducted using B₄H₁₀ (vapor)/Be(CH₃)₂ mole ratios of 0.5, 1.0, and 2.0 to determine the relative rates of Be(CH₃)₂ liquefaction (Table 4). The rate of conversion of Be(CH₃)₂ to liquid products decreased in the order 2.0 > 1.0 > 0.5. A consideration of the instability of B₄H₁₀, however, suggested that these same results could be explained by assuming that the Be(CH₃)₂ liquefaction was initiated by a disproportionation product of B₄H₁₀, most likely B₂H₆, rather than B₄H₁₀ itself. Although the total amount of B₄H₁₀ available for reaction differed during these experiments, the experimental conditions (at mole ratios of 1.0 and 2.0) were such that the actual amount of B₄H₁₀ vapor in contact with the Be(CH₃)₂ was identical at any given time. This was the case because the amount of B₄H₁₀ vapor was governed by the vapor pressure of the liquid boron hydride present. The postulate that B₂H₆, derived from the disproportionation of B₄H₁₀, was initiating the liquefaction of Be(CH₃)₂ was tested experimentally.

C) Influence of B₂H₆ on the B₄H₁₀/Be(CH₃)₂ Reaction. The reaction of Be(CH₃)₂ with mixtures of B₄H₁₀ and B₂H₆ (mole ratio ~ 4:4:1, respectively) resulted in approximately a fourfold decrease in the time required (6 vs 26 hours) for liquefaction of the Be(CH₃)₂ by B₄H₁₀ alone (Table 5). From earlier work on the B₂H₆/Be(CH₃)₂ system (Ref. 1), it is known that the amount of B₂H₆ used was insufficient to cause liquefaction of the beryllium alkyl. Consequently, the increased liquefaction rate observed for the ternary system must be attributed to a reaction involving both B₂H₆ and B₄H₁₀. However, the liquids isolated from these reactions were found to contain significant amounts of methyl groups.

C) Decomposition of B₄H₁₀ During Reaction. The preceding discussion has demonstrated some of the difficulties associated with the use of B₄H₁₀ as a liquefying agent for Be(CH₃)₂, viz:

1. Instability of B₄H₁₀
2. Slow reaction rates
<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>$\text{B}<em>4\text{H}</em>{10}/\text{B}_2\text{H}_6/\text{Be(\text{CH}_3)_2}$ Mole Ratio</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0:1.0:4.2</td>
<td>Liquefaction of the metal alkyl was complete after 6 hours. The reaction time was extended to 8.0 hours, after which time a slightly turbid liquid was formed. By material balance, the average composition of the product was $\text{B}_3\text{H}_7(\text{CH}_3\text{BeH})_2 [(\text{CH}_3)_2\text{Be}]_3 \text{BH}_3$.</td>
</tr>
<tr>
<td>2</td>
<td>4.0:1.0:3.8</td>
<td>Conversion of the Be(\text{CH}_3)_2 to a liquid occurred in 6 hours. No change in the physical state of the reaction mixture was observed after a total reaction time of 7.5 hours. Analyses of the product corresponded to a 39:61 mixture of $\text{B}_3\text{H}_7(\text{CH}_3\text{BeH})_2 [\text{Be}(\text{CH}_3)_2] \text{BH}_3$ and $\text{B}_3\text{H}_7(\text{CH}_3\text{BeH})_4 \text{BH}_2 \text{CH}_3$.</td>
</tr>
<tr>
<td>3</td>
<td>3.9:1.0:3.8</td>
<td>The reaction was run for 15.3 hours. After this time the liquid product had become slightly turbid. By material balance, the average composition of the product was $\text{B}_3\text{H}_7 [\text{Be}(\text{CH}_3)_2]_2 (\text{CH}_3\text{BeH})_2 \text{BH}_3$.</td>
</tr>
</tbody>
</table>
Disproportionation products of \( \text{B}_4\text{H}_{10} \) other than \( \text{B}_2\text{H}_6, \text{B}_3\text{H}_9, \text{B}_5\text{H}_{11}, \) \( \text{H}_2 \), and nonvolatile \((\text{BH})_x\) species. These boron hydrides might also react with the beryllium alkyl, and as a result it was necessary to investigate how their formation might be suppressed.

(C) The use of \( \text{B}_2\text{H}_6 \) to increase the liquefaction rate of \( \text{Be(\text{CH}_3})_2 \) also served to suppress the disproportionation of \( \text{B}_4\text{H}_{10} \). For example, when the stability of a 1:4 mixture of \( \text{B}_2\text{H}_6 \) and \( \text{B}_4\text{H}_{10} \) was tested for 8 hours at ambient temperature, the \( \text{B}_4\text{H}_{10} \) was recovered quantitatively. The recovery of \( \text{B}_4\text{H}_{10} \) from this test was greater than predicted based upon the decomposition of \( \text{B}_4\text{H}_{10} \) vapor at low pressures (40 millimeters, Ref. 7). It was also observed that 31 percent of the \( \text{B}_2\text{H}_6 \) was not recovered from the stability experiment (conducted at a total pressure of approximately 650 millimeters). Conversion of the more stable boron hydride \( \text{B}_2\text{H}_6 \) to \( \text{B}_4\text{H}_{10} \), a known reaction at much higher pressures, must have occurred to replenish any \( \text{B}_4\text{H}_{10} \) which disproportionated (Eq. 1).

\[
\text{2B}_2\text{H}_6 \rightarrow \text{B}_4\text{H}_{10} + \text{H}_2 \tag{1}
\]

Evidence for this type of reaction was the correspondence of unrecovered \( \text{B}_2\text{H}_6 \) and the \( \text{H}_2 \) formed during the stability experiment.

(C) Reaction Time. As a result of the disproportionation of \( \text{B}_4\text{H}_{10} \), the reaction time required for the conversion of \( \text{Be(\text{CH}_3})_2 \) to liquid products decreased with increasing \( \text{B}_4\text{H}_{10}/\text{Be(\text{CH}_3})_2 \) mole ratios. When \( \text{B}_4\text{H}_{10}/\text{Be(\text{CH}_3})_2 \) mole ratios of \( \approx 1.0 \) were used, further hydriding of the liquid products to solids also occurred more rapidly. For example, during an experiment in which the \( \text{B}_4\text{H}_{10}/\text{Be(\text{CH}_3})_2 \) mole ratio was 1.0, the beryllium alkyl was completely liquefied after 26 hours at ambient temperature and remained so until the reaction was stopped after 29.5 hours; unreacted \( \text{B}_4\text{H}_{10} \) (28 percent of the original amount) was present after this time. During a second experiment, using the same mole ratio, solids were obtained when the reaction time was extended to 30 hours. A third experiment, conducted at
a mole ratio of 2.0, demonstrated that the metal alkyl could be converted into liquid products in 18 hours, after which time solids were rapidly formed.

Summary of $\text{B}_4\text{H}_{10}/\text{Be(CH}_3\text{)}_2$ Reactions

(C) The best conditions for the preparation of high-energy BTBH liquids appear to be the use of $\text{B}_4\text{H}_{10}/\text{Be(CH}_3\text{)}_2$ mole ratios of <1.0 and long reaction times. The use of long reaction times appears to be necessary for controlled hydriding of the Be-CH$_3$ bonds. At the same time, however, extended reaction times are apt to yield the greatest amount of $\text{B}_4\text{H}_{10}$ decomposition. It is possible that the action of $\text{B}_4\text{H}_{10}/\text{B}_2\text{H}_6$ mixtures on Be(CH$_3$)$_2$, at different mole ratios and increased reaction times, may yield the amount of hydriding desired. However, because other approaches appeared equally promising, this approach was not investigated.

Conversion of $\text{Be(C}_2\text{H}_5\text{)}_2$ to BTBH Liquids

(C) Because of the physical state of $\text{Be(C}_2\text{H}_5\text{)}_2$, a liquid at ambient temperature, it was anticipated that its reactions with $\text{B}_4\text{H}_{10}$ might be faster and less complex than those between $\text{B}_4\text{H}_{10}$ and Be(CH$_3$)$_2$. Furthermore, the successful preparation of ethyl-substituted BTBH liquids might result in materials with better physical properties.

(C) It was demonstrated under Contract AF04(611)-8550 that the viscosity of BTBH liquids having the general formula $\text{(BH}_3\text{)}_2[(\text{CH}_3\text{)}_{\text{m}}\text{Be}_\text{m+nH}_n\text{x}]$ increased with the degree of polymerization (x) and the hydrogen content (n), (Ref. 1). As a consequence, those liquids yielding the best calculated specific impulse possessed the highest viscosity, as the examples in Table 6 demonstrate.
TABLE 6

SPECIFIC impulse VALUES AND VISCOSITIES OF some BTM species

<table>
<thead>
<tr>
<th>Formula</th>
<th>Specific Impulse $\left(H_2O_2\right)$, seconds</th>
<th>Viscosity Similarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left(\text{BH}_3\right)_2\left(\text{BeH}_2\right)\left(\text{CH}_2\text{BeH}\right)\left(\text{CH}_3\right)_2\text{Be}\right)_4$</td>
<td>324</td>
<td>Honey</td>
</tr>
<tr>
<td>$\left(\text{CH}_3\right)_2\text{Be}\right)_2\left(\text{BeH}_2\right)\left(\text{CH}_3\right)_2\text{Be}\right)_4$</td>
<td>315</td>
<td>Glycerine</td>
</tr>
<tr>
<td>$\left(\text{BH}_3\right)_2\left(\text{BeH}_2\right)\left(\text{CH}_3\right)_2\text{Be}\right)_4$</td>
<td>316</td>
<td>Water</td>
</tr>
</tbody>
</table>

(C) Improvements in the liquid properties of the BTM liquids could conceivably result from the substitution of ethyl for methyl groups. From the viewpoint of energetic materials, however, this modification would be beneficial only if one ethyl group can be used in place of two or more methyl groups. The reaction of $\text{B}_4\text{H}_{10}$ with $\text{Be}\left(\text{C}_2\text{H}_5\right)_2$ served to illustrate the feasibility of this approach. This and other reactions of $\text{Be}\left(\text{C}_2\text{H}_5\right)_2$ are summarized in Table 7.

(C) $\text{Be}\left(\text{C}_2\text{H}_5\right)_2/\text{B}_4\text{H}_{10}$ Reaction. The reaction of $\text{B}_4\text{H}_{10}$ and $\text{Be}\left(\text{C}_2\text{H}_5\right)_2$ occurred readily at ambient temperature to yield the compound $\text{B}_3\text{H}_7\left(\text{C}_2\text{H}_5\text{BeH}\right)\text{BeH}_2\text{Be}\right)_3$ (specific impulse, 326 seconds). Comparison of the most likely molecular compositions of the two compounds $\text{B}_3\text{H}_7\left(\text{C}_2\text{H}_5\text{BeH}\right)\text{BeH}_2\text{Be}\right)_3$ and $\text{B}_3\text{H}_7\left(\text{C}_2\text{H}_5\text{BeH}\right)\left(\text{BeH}_2\right)\text{Be}\right)_3$, for which the degree of polymerization is identical, demonstrates that one ethyl bridge group can be substituted for the two methyl bridge groups in the former compound. Furthermore, an improvement in the theoretical performance is obtained by altering the alkyl group (Table 2). Although both of the above compounds were quite mobile at ambient temperature, the $\text{C}_2\text{H}_5$-substituted material was still a mobile liquid at -40 C at which temperature the $\text{CH}_3$-substituted material was a glass.

(C) $\text{Be}\left(\text{C}_2\text{H}_5\right)_2/\text{B}_4\text{H}_{10}$ Reaction. While the preparation of $\text{B}_3\text{H}_7\left(\text{C}_2\text{H}_5\text{BeH}\right)\text{BeH}_2\text{Be}\right)_3$ demonstrated that ethyl-substituted BTM liquids could be prepared, and that one ethyl group could be substituted for two methyl groups with
TABLE 7

SUMMARY OF Be\((C_2H_5)_2\) REACTIONS
(Conducted at Ambient Temperature)

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Mole Ratio</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_4H_{10}/Be(C_2H_5)_2)</td>
<td>0.55</td>
<td>After a reaction time of 24 hours, a liquid was extracted from the reaction mixture. This material analyzed as (B_3H_7(C_2H_5BeH)BeH_2BH_3).</td>
</tr>
<tr>
<td>(B_2H_6/Be(C_2H_5)_2)</td>
<td>0.8 and 0.4</td>
<td>Rapid hydriding of the metal alkyl occurred. Both Be((BH_4))_2 and impure BeH(_2) were formed during these experiments.</td>
</tr>
<tr>
<td>(Be(BH_4)_2/Be(C_2H_5)_2)</td>
<td>0.8</td>
<td>A volatile liquid was formed which analyzed as (C_2H_5BH_2(C_2H_5BeH)BeH_2BH_3). The material decomposed at ambient temperature to yield (B(C_2H_5)_3) and nonvolatile solids.</td>
</tr>
<tr>
<td>([C_2H_5]_2BH)_2/Be(C_2H_5)_2\</td>
<td>2.0</td>
<td>All attempts to prepare (BeH_2[HB(C_2H_5)_2]_2) by this reaction were unsuccessful. The reaction product decomposed to yield (B(C_2H_5)_3) and nonvolatile solids corresponding to ((BeH_2)_xB(C_2H_5)_3)_2.</td>
</tr>
</tbody>
</table>
some improvement in theoretical performance, it did not show unequivocally the effect of ethyl groups on the fluidity of BTBH liquids. Both the methyl and ethyl compounds in question were triborane terminated, and triborane termination itself results in good fluidity.

(C) Because the reactions of tetraborane appear to parallel those of diborane (compare Eq. 2 and 3), the synthesis of BH$_3$(C$_2$H$_5$BeH)$_2$BH$_3$ from B$_2$H$_6$ and Be(C$_2$H$_3$)$_2$ was attempted (Eq. 5). Comparison of the physical state of this compound with that of BH$_3$(CH$_3$BeH)$_2$BH$_3$ would demonstrate more clearly the effect of ethyl groups on the physical state of BTBH liquids.

\[
\text{Be(CH}_3 \text{)}_2 + 2 \text{B}_2\text{H}_6 \rightarrow \text{BH}_3(\text{CH}_3\text{BeH})_2\text{BH}_3 + \text{boron alkyl byproducts}
\]

(solid; melting point, 48 C) \hspace{1cm} (2)

\[
\text{Be(CH}_3 \text{)}_2 + \text{B}_2\text{H}_4\text{H}_2 \rightarrow \text{BH}_3(\text{CH}_3\text{BeH})_2\text{BH}_3 + \text{boron alkyl byproducts}
\]

(liquid) \hspace{1cm} (3)

\[
\text{Be(C}_2\text{H}_5 \text{)}_2 + \text{B}_2\text{H}_4\text{H}_2 \rightarrow \text{BH}_3(\text{C}_2\text{H}_5\text{BeH})_2\text{BH}_3 + \text{boron alkyl byproducts}
\]

(liquid) \hspace{1cm} (4)

\[
\text{Be(C}_2\text{H}_5 \text{)}_2 + \text{B}_2\text{H}_6 \rightarrow \text{BH}_3(\text{C}_2\text{H}_5\text{BeH})_2\text{BH}_3 + \text{boron alkyl byproducts}
\]

(physical state unknown) \hspace{1cm} (5)

(C) The Be(C$_2$H$_5$)$_2$/B$_2$H$_6$ reaction, when conducted at mole ratios of 1.25 and 2.18, failed to yield any liquid beryllium products. Instead, the reactions proceeded rapidly to form solid boron alkyl-terminated beryllium hydride and Be(BH$_4$)$_2$.

(C) Be(BH$_4$)$_2$/Be(C$_2$H$_5$)$_2$ Reaction. The subsequent approach to the synthesis of a BH$_3$-terminated, ethyl-substituted liquid was the attempted preparation of BH$_3$(C$_2$H$_5$BeH)$_2$BH$_3$ or (C$_2$H$_5$BeH)$_2$BH$_3$. The preparation of this compound was attempted via a method analogous to that used for the synthesis of (CH$_3$BeH)$_2$, i.e., the reaction of the beryllium alkyl with Be(BH$_4$)$_2$ \((1\cdot f. \ 8)\).
(C) Rapid solution of Be( BH₄)₂ by Be(C₂H₅)₂ occurred at ambient temperature, but the reaction product was not the expected (C₂H₅BeBH₄)₂ (Eq. 6).

\[
\text{Be(C₂H₅)₂ + Be(BH₄)₂} \rightarrow (\text{C₂H₅BeBH₄})₂
\]

Instead of (C₂H₅BeBH₄)₂, a volatile liquid compound, BH₃(C₂H₅BeH)BeH₂BH₂C₂H₅ (specific impulse, 311 seconds), was obtained. Based on this reaction and those run between Be(C₂H₅)₂ and other B-H containing materials, it was evident that under comparable conditions, the Be-C₂H₅ bond undergoes hydriding more easily than the Be-CH₃ bond.

(C) Partial characterization was made of BH₃(C₂H₅BeH)BeH₂BH₂C₂H₅. The material exhibited a vapor pressure of 2 mm Hg at 25°C and had a melting point < -40°C. The compound decomposed at ambient temperature, however, to yield B(C₂H₅)₃, and nonvolatile solids.

(C) Reaction of Be(C₂H₅)₂ and Tetraethylidiborane. Based upon the reaction of Be(C₂H₅)₂ and B₂H₆ (described previously), it might be expected that alkyl-
diboranes would also result in the formation of "impure BeH₂". However, the reaction between Be(C₂H₅)₂ and tetraethylidiborane, [BH(C₂H₅)₂]₂, has been reported to yield a stable, liquid complex, BeH₂[BH(C₂H₅)₂]₂ (Ref. 9). Because there was a desire to use BeH₂[BH(C₂H₅)₂]₂ as an intermediate in the formation of BTBH liquids, some effort was directed toward its preparation and isolation.

(C) The previous work conducted at Rocketdyne under Contract AF04(611)-8550 on the Be(C₂H₅)₂/[BH(C₂H₅)₂]₂ system indicated that the initial product formed dissociated to give a volatile compound containing hydrolyzable ethyl groups (Ref. 1). These results suggested the volatilization of Be-C₂H₅ groups in the form of a complex because of incomplete hydriding of the Be-C₂H₅ bonds. Consequently, an experiment was conducted to establish the degree of hydriding of the Be(C₂H₅)₂ by the diborane derivative.

(C) A 2:1 mixture of [(C₂H₅)₂BH]₂ and Be(C₂H₅)₂ was prepared in the high-vacuum system and was permitted to warm from -196°C to ambient temperature. While
warming the mixture to ambient temperature, the following transformations were observed: (1) melting of the components to a clear mobile solution; (2) rapid formation of a precipitate, just below 0°C, sufficiently thick to stop stirring; and (3) rapid dissolution of the solid to yield a clear mobile liquid. Subsequent hydrolysis of this reaction mixture yielded hydrogen containing only 0.1 mole percent ethane. The virtual absence of ethane in the gas formed after hydrolysis indicated a near-quantitative transfer of ethyl groups from beryllium to boron as shown in Eq. 7.

\[
\text{Be(C}_2\text{H}_5)_2 + 2 \text{C}_2\text{H}_5\text{BH}_2 \rightarrow \text{BeH}_2[\text{BH(C}_2\text{H}_5)_2]_2 + 2\text{B(C}_2\text{H}_5)_3 \quad (7)
\]

(C) A duplicate of the preceding experiment was run and efforts were made to isolate the complex shown in Eq. 6. Separation of the byproduct \(\text{B(C}_2\text{H}_5)_3\), was attempted by maintaining the reactor at 0°C while removing the volatile materials by vacuum condensation. The residual material was a clear glass, while the volatiles consisted of a mixture of solid and liquid at -78°C, which converted to a clear liquid at ambient temperature. Analyses of the volatile fraction demonstrated the presence of beryllium, hydrolyzable ethyl groups, hydridic hydrogen and boron; approximately one-half of the beryllium initially present as \(\text{Be(C}_2\text{H}_5)_2\) was found in the volatile fraction. The nonvolatile glass had a Be:B ratio of 3.4:1, and the gas formed after hydrolysis was hydrogen containing only trace amounts of ethane.

(C) Despite the fact that it was demonstrated that hydriding of the \(\text{Be(C}_2\text{H}_5)_2\) by \(\text{BH(C}_2\text{H}_5)_2\) occurred in the stoichiometry shown in Eq. 6, the isolation of the reported nonvolatile \(\text{BeH}_2[\text{BH(C}_2\text{H}_5)_2]_2\) was not possible. Because incomplete hydriding of the beryllium does not appear to be the reason for the failure to isolate the complex, it was concluded that the stability of the complex is marginal. The dissociation of the liquid product to nonvolatile species, most likely boron alkyl-terminated beryllium hydrides, and volatile products other than \(\text{B(C}_2\text{H}_5)_3\) prevented isolation and identification of the initially formed beryllium material. These results are consistent with the more recent studies conducted at Ethyl Corporation on the stability of \(\text{BeH}_2[\text{BH(C}_2\text{H}_5)_2]_2\)/Beane binary systems (Ref. 10).

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Reaction of $B_4H_{10}$ and Alkylberyllium Hydrides

(C) In the absence of solvents, the reaction of $B_4H_{10}$ with $Be(CH_3)_2$ or $Be(CH_2)_2$ can be explained best by a reaction mechanism involving de-polymerization and hydriding of the beryllium dialkyl, and subsequent complexing of the Be-H species by the cleavage products of $B_4H_{10}$ and $B_3H_7$. Because such BTBH liquids as $B_3H_7(CH_3BeH)BeH_2BH_3$ (specific impulse, 326 seconds), $B_3H_7(CH_2BeH)BeH_2BH_3$ (specific impulse, 326 seconds) and other high-energy materials were formed from the reaction of $B_4H_{10}$ and the beryllium dialkyls, it was believed that a better fuel might be produced from the action of $B_4H_{10}$ on the alkyl beryllium hydride or dialkylberyllium-alkylberyllium hydride copolymers. A summary of the reactions investigated is presented in Table 8.

(C) $B_4H_{10}/[(CH_2)_2Be.CH_2BeH]$ Reaction. The ambient temperature decomposition of $Be(CH_2)_2$ (described subsequently) results in the formation of the copolymer $[(CH_2)_2Be.CH_2BeH]_x$. The reaction of this material with $B_4H_{10}$ and with $B_2H_6/B_4H_{10}$ mixtures as a preparative method for ethyl-substituted BTBH liquids was investigated.

(C) The reaction of pure $B_4H_{10}$ with the copolymer at ambient temperature was conducted at a $Be/B_4H_{10}$ ratio of 2.6. Under these conditions, the solid yielded a liquid after 4 days. The only volatile product observed was $B(CH_2)_3$. The average composition of the mobile, nonvolatile liquid product was $B_3H_7(CH_2BeH)_4BeH_2B_3H_7$ (specific impulse, 315 seconds).

(C) $B_4H_{10}/B_2H_6/[(CH_2)_2Be.CH_2BeH]$ Reaction. To increase the rate of reaction of $B_4H_{10}$ with the copolymer and possibly the hydride content of the liquid product as well, a reaction was carried out between the copolymer and a mixture of $B_4H_{10}$ and $B_2H_6$. At a $B_4H_{10}/B_2H_6/Be$ ratio of 3.7:1.0:8.4, the time required to convert the copolymer to a liquid product was reduced to 2 days. Although the $B_2H_6$ served to promote the reaction of the copolymer with $B_4H_{10}$, it also caused the formation of a less polymeric liquid product: $B_3H_7(CH_2BeH)_3BeH_2B_3H_7$ (specific impulse, 317 seconds).

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TABLE 8

SUMMARY OF $B_4H_{10}$/ALKYLBERYLLIUM HYDRIDE REACTIONS
(Conducted at Ambient Temperature)

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Mole Ratio</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_4H_{10}/[(C_2H_5)_2Be\cdot C_2H_5BeH]_x$</td>
<td>0.6*</td>
<td>An ethyl-substituted BHBN liquid, $(B_3H_7)_2(C_2H_5BeH)_2BeH_2$, was isolated from the reaction mixture.</td>
</tr>
<tr>
<td>$B_4H_{10}/B_2H_6/[(C_2H_5)_2Be\cdot C_2H_5BeH]_x$</td>
<td>3.7/1.0/8.4*</td>
<td>The addition of B$_2$H$_6$ caused an increased reaction rate and resulted in the formation of a BHBN liquid with a lower degree of polymerization. Analyses of the liquid corresponded to $(B_3H_7)_2(C_2H_5BeH)_2BeH_2$.</td>
</tr>
<tr>
<td>$B_4H_{10}/(C_2H_5BeH)_x$</td>
<td>0.4*</td>
<td>The reaction proceeded rapidly in toluene to yield insoluble solids, but no liquids.</td>
</tr>
<tr>
<td>$B_4H_{10}/B_2H_6/(CH_3BeH)_x$</td>
<td>2.3/1.0/5.0*</td>
<td>Conversion of the solid (CH$_3$BeH)$_x$ to a liquid occurred in 3 hours. The analyses of the reaction product indicated it to be a 48:52 mixture of $B_3H_7(CH_3BeH)_2[Be(CH_3)_2]_2BeH_2$ and $B_3H_7(CH_3BeH)_6[Be(CH_3)_2]_2BH(CH_3)_2$.</td>
</tr>
</tbody>
</table>

*The calculated values for the polymeric beryllium compounds were based on the monomer.
(C) B₄H₁₀/(C₂H₅BeH)ₓ Reaction. The effect of a solvent on the reaction of B₄H₁₀ and alkylberyllium hydrides was investigated. For this purpose, (C₂H₅BeH)ₓ was chosen because of its solubility in toluene. The results of the reaction illustrated the competitive reactions which can occur in systems of the type studied during the course of this contract.

(C) The reaction of B₄H₁₀ and (C₂H₅BeH)ₓ in toluene yielded only solids, rich in Be-H species, despite the use of a small B₄H₁₀/(C₂H₅BeH)ₓ mole ratio. The failure to obtain liquid products from this reaction is attributed to the hydriding of (C₂H₅BeH)ₓ to (BeH₂)ₓ and the insolubility of the (BeH₂)ₓ in toluene. As a result, the formation and precipitation of (BeH₂)ₓ was a more favored reaction than that involving complexing of the (C₂H₅BeH)ₓ or (BeH₂)ₓ by B₄H₁₀. These results are the same as those obtained from the reaction of liquid B₄H₁₀ and Be(CH₃)₂.

(C) B₄H₁₀/B₂H₆/(CH₃BeH)ₓ Reaction. A B₄H₁₀/B₂H₆ mixture converted (CH₃BeH)ₓ to a liquid in 3 hours when a B₄H₁₀/CH₃BeH/B₂H₆ of 2.34/5.00/1.00 was used. During this reaction time, however, little hydriding of the CH₃BeH occurred; only trace amounts of B(CH₃)₃ were obtained. The principal volatile product was (CH₃BeH₄)₂, suggesting that the B₂H₆ caused some unzipping of the (CH₃BeH)ₓ polymer.

(C) Analyses of the nonvolatile liquid product were best explained by assuming a 48:52 mixture of B₃H₇(CH₃BeH)₆[Be(CH₃)₂]₂B₃H₇ and B₃H₇(CH₃BeH)₆[Be(CH₃)₂]-BH(CH₃)₂. Because end-group analyses for boron of the (CH₃BeH)ₓ, prepared from (BeH₂)ₓ [B(C₂H₅)₃]₂ and Be(CH₃)₂, had indicated a degree of polymerization of 26, there was little doubt that its reaction with the B₄H₁₀/B₂H₆ mixture had caused chain-shortening. The failure to obtain a more hydrided BTBH liquid than observed was thought to be the consequence of the short reaction time used. To test this postulate, a sample of the B₄H₁₀/B₂H₆/(CH₃BeH)ₓ reaction products was treated with an additional quantity of B₂H₆ and B₄H₁₀ for 2.5 hours. The resulting compound analyzed as B₃H₇(CH₃BeH)₆BH₂CH₃.
Problems of Hydriding BTH Liquids

(C) The reaction of $\text{BH}_4\text{H}_2$ or $\text{BH}_6/\text{BH}_6$ mixtures with alkylberyllium hydrides failed to yield BTH liquids of significantly greater hydridic hydrogen contents than those obtained from similar reactions with dialkylberyllium compounds. These observations may be a consequence of a combination of several factors.

(C) X-ray data indicate that the angles in the four-membered rings of the $\text{Be(CH}_3)_2$ chains are $\text{Be-C-Be, 66 degrees and C-Be-C, 114 degrees.}$ Although no structural data exist for $(\text{BeH}_2)_x$, it is presumed that the $\text{Be-H-Be}$ angle should be greater than 66 degrees and the $\text{H-Be-H}$ angle should be less than 114 degrees because of the better orbital overlap of the spherical $\text{sp}^3$ orbital of $\text{H}$ with the two beryllium $\text{sp}^3$ orbitals when compared with the overlap of the narrower $\text{sp}^3$ orbital of carbon.

(C) On this basis, an explanation for the facile replacement of approximately one-half of the methyl groups in $\text{Be(CH}_3)_2$ (I) by hydrogen may be invoked.

![Diagram](image)

When one of the two bridging $\text{CH}_3$ groups of $\text{Be(CH}_3)_2$ is replaced by $\text{H}$, to give structure III, the tendency is for the $\text{Be}$ atoms to move closer together, reducing the $\text{Be-C-Be}$ angle to less than 66 degrees. The resulting increased overlap of the three $\text{sp}^3$ orbitals makes a stronger methyl bridge bond, and as a result, one more difficult to replace in structure III than in structure I. Consequently, even though the formation of $\text{BeH}_2$ (II) units should be favored thermodynamically, replacement of the remaining $\text{CH}_3$ by $\text{H}$ becomes kinetically controlled. Potential solutions to this problem are outlined in the Summary and Recommendations section of this report.
Reactions of Metathetical (BeH₂)ₓ

(C) Several attempts were made to prepare BTBH liquids from the reaction of metathetical (BeH₂)ₓ, synthesized from the reaction of Al(C₂H₅)₃ and Be(BH₄)₂ (Ref. 11), and boron-hydrogen containing compounds. While reactions were observed in the systems investigated, none led to the isolation of a liquid beryllium compound.

(C) B₄H₁₀/(BeH₂)ₓ Reaction. The work performed on the reactions of boron hydrides and beryllium alkyls demonstrated that the preparation of liquid beryllium compounds with specific impulses >310 seconds is easily achievable (Ref. 1). However, a different approach to the formation of BTBH liquids of higher specific impulse values might result from the reaction of B₄H₁₀, for example, with (BeH₂)ₓ.

(C) The reaction of B₄H₁₀ and (BeH₂)ₓ at ambient temperature during 4 days resulted in the formation of H₂ and Be(BH₄)₂, but no liquids. The yield of Be(BH₄)₂ was 20 percent (based on the beryllium hydride used), with only a 25 percent recovery of the B₄H₁₀ used. The formation of Be(BH₄)₂ from B₄H₁₀ and (BeH₂)ₓ at ambient temperature was undoubtedly caused by the formation of H₃ groups via the decomposition of B₄H₁₀.

(C) 1,2-Trimethylenediborane/BeH₂ Reaction. The reaction of 1,2-trimethylenediborane (Ref. 12)

![Diagram of 1,2-Trimethylenediborane](image)

and metathetical (BeH₂)ₓ was also investigated as a method for forming BTBH liquids. Although the reactions of Be(BH₄)₂ (Ref. 8), B₂H₆ (Ref. 8), and B₄H₁₀ with metathetical (BeH₂)ₓ yielded only sublimable solid products, the presence of methylene groups in the 1,2-trimethylenediborane could serve to alter the physical state of the products.
A mixture of the diborane derivative (containing some n-propyldiborane, a byproduct of the preparation of 1,2-trimethylenediborane) and metathetical (BeH₂)x formed a thick paste at ambient temperature which exhibited no apparent change after 16 hours. Heating the mixture at 57 °C for 4 hours resulted in the formation of a volatile solid, Be(H₄)₂. No further investigation of this system was made because the main portion of the reaction mixture remained a pasty solid.

ALANE-TERMINATED BERYLLIUM LIQUIDS

As a result of experiments conducted at Rocketdyne under Contract AF04(611)-9882, it was determined that Beane reacted with Al(CH₃)₃ at elevated temperatures, and that concentration of the reaction products afforded a liquid product containing both beryllium and aluminum (Ref. 13). Although performance calculations indicate that the BTBH liquids are potentially higher-performing neat fuels than the alane-terminated beryllium hydrides (ATBH) liquids, the latter materials have other applications including:

1. Use as liquid carriers for Beane in heterogeneous propellants
2. Precursors for BTBH liquids

Since initiation of work on the present contract, gelled systems of ATBH and Beane have been prepared (Ref. 2). Further exploitation of the use of ATBH liquids in heterogeneous systems is being investigated under Contract F04611-67-C-0038 (Ref. 14). The following discussion is, therefore, confined to investigations concerning the preparation of ATBH liquids and their interaction with boron-containing compounds.

Reaction of Beane With Al(CH₃)₃

The reaction of Beane with Al(CH₃)₃ was observed to be time and temperature dependent; at temperatures below 120 °C the rate of reaction was quite slow. A determination was made of the rate of reaction between Beane and Al(CH₃)₃.
at 130 °C by conducting a series of experiments in which 2:1 mixtures of 
Al(CH₃)₃ and Beane (96 percent purity) were used. The rate of dis-
appearance of solid Beane (Fig. 1) fitted a simple second-order expres-
sion (as determined by the method presented in Ref. 15), although the 
significance of this is not known. As shown by the plot in Fig. 1, the 
disappearance of the Beane was near-quantitative (98.6 percent) after 
48 hours.

(C) The preliminary experiments resulted in no evidence for the formation of 
noncondensable gases during the reaction of Beane with Al(CH₃)₃ [Contract 
AF04(611)-9882]. The liquid product isolated, however, had an analytically 
established H:Be ratio less than 2, suggesting that reaction of the Beane 
was accompanied by hydrogen-methyl group exchange. The low H:Be ratio 
would then arise from the removal of Al-H species during the isolation of 
the main product.

(C) An experiment was performed to determine if any Al-H species could be 
identified among the volatile products from the Al(CH₃)₃/Beane reaction. 
After heating a 1.7:1 mixture of Al(CH₃)₃ and Beane at 120 °C for 24 hours, 
the volatile materials were removed by vacuum distillation. Analyses of 
the volatile products revealed the presence of a hydrogen-containing 
aluminum species, most likely [(CH₃)₃AlH]₃, along with unreacted Al(CH₃)₃. 
The results of this experiment strongly suggest that the reaction of 
Al(CH₃)₃ and Beane occurs as a consequence of hydrogen-methyl group 
exchange.

(C) Composition vs Reaction Time. The series of experiments used for estab-
lishing the rate of reaction of Beane with Al(CH₃)₃ also served to indi-
cate the variation of composition of the ATEH liquids with reaction 
time. While there was some scatter in the analytical data obtained with 
the ATEH materials, i.e., after removal of the excess Al(CH₃)₃ and any 
volatile reaction products, a trend toward decreased methyl group content 
in the ATEH material with reaction time was apparent. However, the best 
product still contained too much carbon for its use as a neat liquid fuel.
Figure 1. Rate of BeH$_2$ Reaction With Al(CH$_3$)$_3$ at 130 °C
(C) Nature of Insoluble Materials. As stated previously, the rate of reaction between Beane and Al(CH₃)₃ is temperature dependent; for example, appreciable amounts of unreacted solids remained after short reaction times even at 150°C (Fig. 1). The nature of the unreacted solids remaining after reaction of Al(CH₃)₃ and Beane (2.3:1 mole ratio) at 120°C for 16 hours was investigated. Isolation and analyses of the insoluble material revealed it to be unreacted Beane of a purity similar to that used (92 vs 96.6 weight percent). These data suggest that the formation of long-chain, insoluble species of the type (BeH₂)ₓ[Al(CH₃)₃]₂ is not a part of the reaction sequence. Reaction via monomeric units or short chains of Beane may accordingly be important in the reaction mechanism.

Reaction of Beane and Dimethylalane

(C) Dimethylalane, [(CH₃)₂AlH]₃, reacts more slowly with Beane than does trimethylalane. A direct comparison of the reactivities of the two alanes was made using 2:1 alane-to-Beane mixtures. After 24 hours at 150°C, the amount of reaction was four times greater with Al(CH₃)₃ than with the [(CH₃)₂AlH]₃ (21% vs 84% weight percent BeH₂ reacted.) The recovered ATBH liquid was quite viscous and complete removal of the excess dimethylalane from the product was not possible.

(C) A reasonable explanation for the difference in behavior of the two alanes toward Beane is the chemical bonding involved. Assuming the Beane/alane reaction mechanism to involve monomeric species of the alane, the formation of such intermediates from [Al(CH₃)₃]₂ should be easier than from [(CH₃)₂AlH]₃ because Al-H-Al bridge bonds are stronger than Al-CH₃-Al bridge bonds. On this basis, the greater reactivity of Al(CH₃)₃ was not unexpected.

Physical Properties of ATBH Liquids

(C) The molecular structure of the ATBH liquids was assumed to be composed of chains of beryllium atoms appropriately connected by methyl and/or hydrogen...
bridge bonds and terminated by aluminum alkyls. Evidence for this type of structure was based on the existence of known alkylalane complexes containing one unit of BeH₂ (for example, Ref. 16), and the fact that infrared spectra of these materials are not composite spectrograms of (CH₃)₃Al or (CH₃)₂AlH and BeH₂ or CH₃BeH.

(c) Measurements of some physical properties of selected ATBH liquids have been made (Ref. 2), and the data are presented in Table 9.

**TABLE 9**

SOME PHYSICAL PROPERTIES OF (CH₃)₃Al(CH₃BeH)(BeH₂)₂Al(CH₃)₃

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (29 C), g/cm³</td>
<td>0.72</td>
</tr>
<tr>
<td>Thermal Stability (as gas evolution rate), cm³/min/lb</td>
<td>5.1 x 10⁻² (71 C or 160 F)</td>
</tr>
<tr>
<td></td>
<td>1.2 x 10⁻⁴ (ambient temperature)</td>
</tr>
<tr>
<td>Specific Impulse (shifting equilibrium, 1000 - 14.7 psia, H₂O₂), seconds</td>
<td>297</td>
</tr>
</tbody>
</table>

It has been observed that the viscosity of the ATBH material can be varied simply by the addition or removal of Al(CH₃)₃ from the complex. This indicates that the ATBH liquids can participate in an equilibrium of the type exemplified by Eq. 8, although simple dilution of the complex cannot be ignored.

$$[\text{Al(CH₃)₃}]_2 + (\text{CH₃})_3\text{Al(CH₃BeH)}_2\text{(BeH₂)}_2\text{Al(CH₃)₃} \rightleftharpoons 2(\text{CH₃})_3\text{Al[(CH₃BeH)(BeH₂)]Al(CH₃)₃}$$

Hydriding of ATBH Liquids

(c) The quantitative reaction of Al(CH₃)₃ and BeH₂ in a 2:1 mole ratio and at a temperature of 130 C did not result in a liquid fuel with a specific impulse of ≥ 330 seconds. Therefore, attempts were made to improve the hydridic hydrogen contents of the ATBH liquids by reaction with boron
hydrides and their derivatives. The net result of these reactions was not only partial replacement of the methyl groups by hydridic hydrogen, but also a near-quantitative displacement of the aluminum by boron.

(c) The relative hydriding ability of \( \text{B}_2\text{H}_6 \), \( \text{B}_4\text{H}_{10} \), and \( \text{Be} (\text{BH}_4)_2 \) on a single ATBH liquid was investigated. The improvement in the Be:H values was based upon the initial Be:H:CH\(_3\) values determined for the ATBH liquid being used. A comparison of the results (Table 10) indicated that the reactivity of the three hydriding agents with the ATBH material decreased in the order \( \text{B}_4\text{H}_{10} > \text{Be} (\text{BH}_4)_2 > \text{B}_2\text{H}_6 \). In regard to the displacement of aluminum, the three reagents appeared to be equally effective, i.e., 80 to 85 percent of the aluminum was recovered as a methyl-substituted aluminum borohydride.

**TABLE 10**

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Quantity, millimoles</th>
<th>Be:H:CH(_3) Ratio ATBH Liquids</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{B}<em>4\text{H}</em>{10} )</td>
<td>0.429</td>
<td>1.0:1.0:1.85</td>
<td>1.0:2.9:1.0</td>
</tr>
<tr>
<td>( \text{Be} (\text{BH}_4)_2 )</td>
<td>0.452</td>
<td>1.0:1.0:1.85</td>
<td>1.0:1.8:0.92</td>
</tr>
<tr>
<td>( \text{B}_2\text{H}_6 )</td>
<td>0.455</td>
<td>1.0:1.0:1.85</td>
<td>1.0:1.5:0.93</td>
</tr>
</tbody>
</table>

**Improved Preparations of Beryllium Alkyls**

(U) The \( \text{Be} (\text{CH}_3)_2 \) and \( \text{Be} (\text{C}_2\text{H}_5)_2 \) used in the preceding reactions were prepared by the Grignard procedure, and great care was taken in purifying these materials before use. Vacuum sublimation of \( \text{Be} (\text{CH}_3)_2 \) from the magnesium salts formed during the preparative reaction often resulted in the cosublimation of an iodide-containing impurity (most likely CH\(_3\)BeI). It was found that the iodide impurity could be converted to a nonvolatile substance by thermally soaking the crude product at 115°C. Subsequent sublimation of the \( \text{Be} (\text{CH}_3)_2 \) then yielded material of 99+ percent purity.
A convenient procedure for the preparation of ether-free Be(C$_2$H$_5$)$_2$ was developed during the course of this contract. It was found that if the solid reaction products of C$_2$H$_5$MgBr and BeCl$_2$ were extracted with benzene at ambient temperature, the Be(C$_2$H$_5$)$_2$ which was recovered after a simple distillation was of 99+ percent purity. The benzene extraction was found to facilitate the recovery of the Be(C$_2$H$_5$)$_2$ from the solid reaction products.

DECOMPOSITION OF Be(C$_2$H$_5$)$_2$ AT AMBIENT TEMPERATURE

Although Be(C$_2$H$_5$)$_2$ undergoes pyrolysis at elevated temperatures (Ref. 17), no report of its instability at ambient temperature is cited in the literature. However, during the course of the present research effort, a slow decomposition of the metal alkyl was observed to occur at ambient temperature. The decomposition products of Be(C$_2$H$_5$)$_2$ consisted of a beryllium-containing solid and unidentified gases. Analyses of the solid revealed it to be a copolymer of Be(C$_2$H$_5$)$_2$ and C$_2$H$_5$BeH,[(C$_2$H$_5$)$_2$Be·C$_2$H$_5$BeH]$_x$.

It has been observed at Ethyl Corporation that the binary system Be(C$_2$H$_5$)$_2$/Beane slowly solidifies on standing at ambient temperature (Ref. 10). Furthermore, Beane coated with basic polymers such as Carbowax 1000, Epoxy resin, and polyesters when mixed with Be(C$_2$H$_5$)$_2$ produced solids within a few days. The similarity between the behavior of neat Be(C$_2$H$_5$)$_2$, prepared by the Grignard method, which undoubtedly contained trace amounts of diethyl ether, and the Ethyl Corporation results suggests that the decomposition of Be(C$_2$H$_5$)$_2$ is catalyzed by Lewis bases.

PYROLYSIS OF Be(C$_2$H$_5$)$_2$

The pyrolysis of Be(C$_2$H$_5$)$_2$ has been reported to yield a liquid compound having the composition C(BeH$_2$·BeC$_2$H$_5$)$_4$ (Ref. 17). Because this compound represents a class of liquid fuels containing beryllium and hydrogen, but has no extraneous terminating groups, some effort was expended in attempting to prepare a pure sample of this material. Several
Samples of a nonvolatile liquid product were obtained from the pyrolysis of Be(C$_2$H$_5$)$_2$ at 200°C. Although the ratios of the constituents of the pyrolysis product approached those expected for the composition C(BeH$_2$BeC$_2$H$_5$)$_4$, in no case was a pure sample obtained.

(U) The failure to purify the liquid pyrolysis product by distillation appears to have been caused by the codistillation of a high-molecular-weight hydrocarbon formed during the pyrolysis. Mass spectral analyses of the ambient temperature volatile hydrocarbon byproducts disclosed not only ethane and ethylene (the principal products), but also hydrocarbons up through substituted pentanes. The formation of the hydrocarbons other than ethane and ethylene is attributed to the Be(C$_2$H$_5$)$_2$ acting as a Ziegler-type polymerization catalyst for ethylene. The formation of still higher hydrocarbons of low volatility resulted in the formation of an intractable mixture containing the desired beryllium product.

(U) Deuterolysis was used to demonstrate that the hydrocarbon was present as a physical contaminant rather than as a high-molecular-weight beryllium alkyl species. Deuterolysis of a distilled sample of the pyrolysis product did not yield any hydrocarbons heavier than methane and ethane containing C-D bonds as would be expected if they were chemically bound to the beryllium.
CONCLUSIONS AND SUMMARY

(C) This program has demonstrated that liquid beryllium hydrides may be prepared with theoretical specific impulses approaching 330 seconds (1000 - 14.7, H₂O₂ oxidizer). It appears that higher borane fragments, such as B₃H₇, are better than simple BH₃ groups as the terminating species for these liquids, inasmuch as liquids containing B₃H₇ have good fluidity and other satisfactory properties coupled with high impulse. Further increases in BeH₂ content are needed for the liquid beryllium hydrides to surpass the 330-second specific impulse level.

(C) A summary of the important results supporting the above conclusions, as well as other aspects of this work, are as follows:

1. Reactions of B₄H₁₀ with Be(CH₃)₂ and Be(C₂H₅)₂ resulted in the synthesis of compounds such as B₃H₇(CH₃BeH)₂BeH₂BH₃ (329 seconds), B₃H₇(C₂H₅BeH)BeH₂BH₃ (326 seconds), B₃H₇(CH₃BeH)₃BeH₂BH₃ (326 seconds), and B₃H₇(CH₂BeH)₂BH₃ (320 seconds).

2. Previously it had been observed that the termination of BTBH liquids with two BH₃ groups often yielded materials which underwent reversible dissociation. When one of the BH₃ groups was replaced by a B₃H₇ terminator, the tendency of the liquids to dissociate reversibly was eliminated.

3. The preparation of B₃H₇(C₂H₅BeH)BeH₂BH₃ demonstrated that it is possible to prepare ethyl-substituted BTBH analogs of previously known methyl-substituted liquids, and that one ethyl group replacing two methyl groups in such compounds leads to higher specific impulse.

4. The preparation of liquids containing both ethyl and B₃H₇ groups demonstrated that such compounds have good viscosities and low melting points.
5. The conversion rate of solid beryllium compounds to liquids by $B_4H_{10}$ was greatly increased by the use of $B_2H_6/B_4H_{10}$ mixtures. Possibly, the $B_2H_6$ served as a depolymerization agent for $Be(CH_3)_2$ and in so doing rendered the metal alkyl more reactive toward $B_4H_{10}$.

6. Neat $B_4H_{10}$ reacted slowly with $Be(CH_3)_2$. Because of the instability of $B_4H_{10}$ and the slowness of its reaction with $Be(CH_3)_2$, products in addition to the triborane-terminated materials were formed. The disproportionation of $B_4H_{10}$, however, was suppressed when $B_2H_6/B_4H_{10}$ mixtures, rather than pure $B_4H_{10}$, were used.

7. The very reactive hydriding agents $B_2H_6$ and $Be(BH_4)_2$ reacted with $Be(C_2H_5)_2$ and resulted in extensive hydriding of the beryllium. Under comparable experimental conditions, the extent of hydriding $Be(CH_3)_2$ was much less.

8. The preparation of ATEH liquids from Beane and methylated alanes was investigated. Experimental conditions were established for the quantitative reaction of $Al(CH_3)_3$ and Beane.

9. The reaction of ATEH liquids with $B_2H_6$, $B_4H_{10}$, and $Be(BH_4)_2$ proved the feasibility of using the ATEH liquids as precursors for BTEH materials. In each of the preceding reactions, the displacement of aluminum from the ATEH liquids by the B-H containing reagents was greater than 80 percent.

10. It was discovered that extremely pure $Be(C_2H_5)_2$ undergoes decomposition at ambient temperature. The beryllium-containing decomposition product was found to have the composition $[(C_2H_5)_2Be\cdot C_2H_5BeH]_x$ and was subsequently converted to liquids when reacted with $B_4H_{10}$ and/or $B_4H_{10}/B_2H_6$ mixtures.
RECOMMENDATIONS

(C) The preparative route to the B\textsubscript{3}H\textsubscript{7}-terminated liquids has been the reactions of B\textsubscript{4}H\textsubscript{10} with various beryllium compounds. These reactions have proved to be very complex. On the other hand, reactions of the ternary system B\textsubscript{2}H\textsubscript{6}/B\textsubscript{4}H\textsubscript{10}/Be compound are less complex. It is recommended that additional work be performed on these ternary systems. This effort would include a determination of the optimum B\textsubscript{2}H\textsubscript{6} concentration, and its variation, if any, from one alkyl to another; and the optimum reaction time for maximum hydriding of the beryllium compound consistent with formation of serviceable liquid propellants.

(C) The second important aspect of the tetraborane system should be based upon increasing the hydrogen content of the known triborane-terminated liquids. This may be approached in several ways. One method would be the treatment of the known liquids with metathetical BeH\textsubscript{2}, a reaction which occurs readily with borane-terminated liquid compounds.

(C) Another approach would be based on the observation that the formation of Be-H bonds from Be(C\textsubscript{2}H\textsubscript{5})\textsubscript{2} occurs much more readily than from Be(CH\textsubscript{3})\textsubscript{2}. This difference in the reactivity of Be(CH\textsubscript{3})\textsubscript{2} and Be(C\textsubscript{2}H\textsubscript{5})\textsubscript{2} may serve a useful purpose if instead of reacting B\textsubscript{4}H\textsubscript{10}, for example, with either pure Be(CH\textsubscript{3})\textsubscript{2} or Be(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}, a mixed alkyl, CH\textsubscript{3}BeC\textsubscript{2}H\textsubscript{5}, or a copolymer of the two alkyls is used. The reaction of either one of these materials with a B\textsubscript{2}H\textsubscript{6}/B\textsubscript{4}H\textsubscript{10} mixture may result in a rapid and quantitative conversion of the Be-C\textsubscript{2}H\textsubscript{5} bonds to Be-H bonds, leaving the Be-CH\textsubscript{3} bonds to serve as the groups that maintain liquid properties in the products.

(C) Alternate methods to the preparation of triborane-terminated liquids should also be developed. The three reagents B\textsubscript{2}H\textsubscript{6}, Be(CH\textsubscript{3})\textsubscript{2}, and B\textsubscript{4}H\textsubscript{10} all react with concentrated ATBH materials and result in displacement of the alane terminators. Additional reactions, as shown by the following equations, may also be feasible.

\[ 2\text{Base}.B_{3}H_{7} + \text{ATBH liquid} \rightarrow \text{BTBH liquid} + 2\text{Base}.Al(CH_{3})_{3} \]
The above reactions may not only prove to be more convenient than those involving $B_4H_{10}$ and beryllium alkyls, but may also result in the formation of pure liquid beryllium compounds, free from side products introduced from the disproportionation of $B_4H_{10}$.

(C) Two additional approaches to the preparation of $B_{10}E$ liquids are outlined below. These reactions are considered exploratory and would be given a lower priority than those presented above.

1. In the case of $B_4H_{10}$, it is believed that the bulkiness of the $B_3H_7$ group helps prevent the triborane-terminated species from crystallizing. Similarly, $B_9H_9$ and $B_{11}H_{11}$ could yield bulky fragments, $B_4H_6$ and $B_4H_8$ respectively, which might serve as terminators and impart good physical properties to liquid beryllium fuels. The reactions of the pentaboranes with polymeric beryllium compounds should be explored.

2. The use of difunctional boranes such as 1,2-trimethylenediborane, $H_2BC_3H_6BH_2$, to link Be-Be segments and impart flexibility to the chain, did not yield $B_{10}E$ liquids on reaction with metathetical $BeH_2$. However, more desirable reactions may result from the action of these materials on beryllium alkyls.
EXPERIMENTAL DETAILS

GENERAL

(U) Handling and manipulation of pyrophoric and/or toxic materials were performed in high-vacuum systems or inert-gas, gloved boxes. Most reactions were conducted in round-bottom Pyrex reactors of varying volumes, fitted with Fischer-Porter needle valves. These reactors were connected to the high-vacuum systems by means of standard-tapered joints.

Chemicals

(U) **Be(BH₄)₂.** Beryllium borohydride was prepared by reacting LiBH₄-KBH₄ mixtures with BeCl₂ (Ref. 11).

(U) **Beryllium Alkyls.** Dimethylberyllium was prepared by the method of Gilman (Ref. 18). After thermal dissociation of the Be(CH₃)₂ etherate, iodide impurities were detected in the sublimed Be(CH₃)₂. Removal of this contaminant, possibly CH₃BeI, was accomplished by thermally soaking the crude Be(CH₃)₂ at 115 °C. Subsequent sublimation of the material treated in this manner yielded pure Be(CH₃)₂.

(U) **Ether-free Be(C₂H₅)₂.** was prepared by a modification of Goubeau’s method (Ref. 17). Modification of Goubeau’s procedure consisted of a benzene extraction of the solid mass formed from the Grignard reaction. Distillation of the benzene extract, after removal of the hydrocarbon, yielded Be(C₂H₅)₂ (boiling point, 69 °C at 0.11 mm Hg) in 55 percent yield and 99+ percent purity.

(U) **B₁₀H₄.** Tetraborane was synthesized by the decomposition of B₂H₆ under pressure essentially as described by Kodama (Ref. 19). As determined by infrared spectroscopy, the material was pure after fractional condensation.
Solvents. Solvents were obtained from various commercial sources, dried over LiAlH₄ and stored over LiAlH₄ until used.

ANALYTICAL PROCEDURES

The gases evolved after acid hydrolysis were removed to a known volume of the high-vacuum system, by means of a Toepler or Sprengel pump, and measured. The gases were assayed, by mass spectrometric techniques, and the relative amounts of hydrogen and CH₄ or C₂H₆ were determined. The amount of hydrocarbon found was presumed to be a direct measurement of the bridging alkyl group content. The hydrolysate was then analyzed for Be and B or Al.

The most reliable analytical results for beryllium were obtained by atomic absorption spectrophotometry. Precipitation of the beryllium as the cupferronate yielded consistently low results. Boron was determined as described in Ref. 1. An alternate analysis (Ref. 20), a rapid flame spectrophotometric procedure, was utilized late in the program and was found to yield equally reliable results. Aluminum was determined gravimetrically by the use of 8-hydroxyquinoline.

In most instances, no direct measurement was made of the alkyl substituents bound to boron. Instead, the extent of boron substitution was determined by the difference between the sum of the weights of the directly measured constituents and the weight of the analytical sample. In the remaining instances, the following procedure was used to determine directly the amount of boron-alkyl substitution.

Direct B-Alkyl Group Analysis

The analysis of BTBH liquids for boron-bound alkyl groups was developed with mixtures of Be(CH₃)₂ and B₂H₆. The procedure was as follows. Weighed samples of Be(CH₃)₂ (0.0420 gram) and B₂H₆ (0.0261 gram) were sealed into a bulb to which were attached, by magnetic break-seals, two reagent ampoules.
One ampoule contained a mixture of xylene (2.0 milliliters) and 12 N HCl (0.6 milliliter) and the second contained propionic anhydride (4.0 milliliters). The $\text{B}_2\text{H}_6/\text{Be(CH}_3)_2$ mixture was reacted for 18.5 hours to ensure equilibration of the CH₃ groups between beryllium and boron species in the liquid product.

(U) The analysis was initiated by introducing the xylene/aqueous acid mixture onto the synthesized liquid complex. The gases formed at ambient temperature were collected, after passing through a -196 C trap, and measured in an automatic Toepler system. All materials not passing -196 C were returned to the bulb, and the bulb was resealed and heated at 125 C for 16 hours to ensure completion of the hydrolysis. Any additional gases formed were again collected.

(U) All remaining volatiles were resealed in the bulb and the propionic anhydride was introduced at ambient temperature. Cleavage of the B-CH₃ bonds by propionic acid was accomplished during 16 hours at 140 C. As previously, the gases produced were passed through a -196 C trap, collected, and measured. Mass spectrometric analyses of the gaseous products were then performed. The accuracy of the analyses is demonstrated by the following data. Calculated were: Be, 1.07 matoms; B, 1.89 matoms; hydridic hydrogen, 5.66 mmoles; and total CH₃ groups, 2.14 mmoles. Found were: Be, 1.02 matoms; B, 1.89 matoms; hydridic hydrogen, 5.60 mmoles; and total CH₃ groups, 2.18 mmoles.

$\text{B}_4\text{H}_{10}/\text{Be(CH}_3)_2$ REACTIONS

Physical State of B₄H₁₀ and its Reactivity

(C) The experiments conducted to determine how the physical state of B₄H₁₀ altered its reaction with Be(CH₃)₂ were performed in the following manner. To a heavy-wall cylindrical reactor containing Be(CH₃)₂ (0.3535 gram, 9.05 mmols) was added liquid B₄H₁₀ (0.47794 gram, 8.00 mmoles). During
the second experiment, Be(CH$_3$)$_2$ (0.3577 gram, 9.15 mmoles) was added to one arm of a heavy-wall inverted Y-reactor and liquid B$_4$H$_{10}$ (0.4764 gram, 8.94 mmoles) condensed in the second arm of the reactor.

(C) Total liquefaction of the Be(CH$_3$)$_2$ in the vapor-phase reaction occurred in 26 hours. The liquid-phase reaction after this same time yielded primarily solids suspended in the unreacted B$_4$H$_{10}$ and alkylboron products. The results of the reactions are presented in Table 11.

### TABLE 11

**REACTION OF Be(CH$_3$)$_2$ WITH B$_4$H$_{10}$ VAPOR AND WITH LIQUID B$_4$H$_{10}$**  
(Reaction Time 29.5 hours at Ambient Temperature)

<table>
<thead>
<tr>
<th>Reactants, mmoles</th>
<th>Volatile Products,* mmoles</th>
<th>Nonvolatile Products, grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$</td>
<td>(CH$_3$)$_2$B$_2$H$_4$</td>
</tr>
<tr>
<td>Be(CH$_3$)$_2$, 9.15</td>
<td>2.50</td>
<td>1.13</td>
</tr>
<tr>
<td>B$<em>4$H$</em>{10}$ (vapor), 8.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Be(CH$_3$)$_2$, 9.05</td>
<td>2.08</td>
<td>--</td>
</tr>
<tr>
<td>B$<em>4$H$</em>{10}$ (liquid), 8.99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*In addition to the tabulated volatile products, trace amounts of (CH$_3$BeBH$_3$)$_2$, Be(BH$_4$)$_2$, and an unstable material, believed to be a methyl-substituted beryllium borohydride, were obtained during both experiments.

(C) Analysis of a sample (0.0268 gram) of the liquid obtained from the vapor-phase reaction yielded H$_2$ (2.67 mmoles), B (0.0108 gram, 1.0 matom), Be (0.0058 gram, 0.64 matom), and CH$_3$(0.35 m mole). The observed Be:B:H:CH$_3$ ratios were 3.84:6.00:16.0:2.10; calculated for [(CH$_3$)$_3$B$\cdot$H$_4$]$\cdot$(BeH$_2$)$_2$[(CH$_3$)$_3$BeH]$_2$ were 4:6:16:2.
Variation of $B_4H_{10}/Be(CH_3)_2$ Mole Ratio and Reaction Time

(C) The data presented in Table 12 summarize the results obtained when the $B_4H_{10}/Be(CH_3)_2$ mole ratio and the reaction time were varied. Analyses of the liquid products obtained from experiments No. 2, 4, and 5 were as follows.

(C) Liquid Product, Experiment 2. Hydrolysis of a 0.0268 gram sample yielded $H_2$ (2.67 mmoles), B (0.0108 gram, 1.0 matom), Be (0.0058 gram, 0.64 matom), and $CH_4$ (0.35 mmole). The Be:B:H:CH ratios were 3.84:6.00:16.0:2.10; calculated for $(CH_3)_3B(H_2)(BeH_2)_2(CH_3BeH)_2$ were: 4:6:16:2.

(C) Liquid Product, Experiment 4. The liquid product was first extracted with n-hexane. The hexane filtrate was concentrated and the residual liquid material was analyzed. Hydrolysis of a 0.0357-gram sample yielded $H_2$ (4.12 mmoles), B (0.0129 gram, 1.19 matoms), Be (0.0081 gram, 0.90 matom), and $CH_4$ (0.50 mmole). The Be:B:H:CH ratios derived from these results were: 3.02:4.00:13.8:7; calculated for $B_3H_3(CH_3BeH)_2BeH_2BH_3$ were: 3:4:15:2.

(C) Liquid Product, Experiment 5. The liquid product was processed in the same manner as for experiment No. 4. Subsequent hydrolysis of a 0.0418-gram sample yielded: $H_2$ (4.07 mmoles), B (0.0153 gram, 1.41 matoms), Be (0.0063 gram, 0.70 matom), and $CH_4$ (0.60 mmole). The Be:B:H:CH ratios of 2.00:4.04:11.6:1.72 approached those calculated for $B_3H_3(CH_3BeH)_2BH_2CH_3$, i.e., 2:4:12:2.

$B_4H_{10}/B_2H_6/(CH_3)_2Be$ Reactions

(C) A summary of the reaction products formed from the titled reaction is presented in Table 12. Of these products, only the liquid from experiment No. 2 was analyzed. The compositions of the remaining two liquids were


**TABLE 12**

**VARIATION OF \( B_4H_{10} \) (VAPOR) /Be\((CH_3)_2\) MOLE RATIO AND REACTION TIME**

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Reactants, moles</th>
<th>Reaction Time, hours</th>
<th>Volatile Products, moles</th>
<th>Nonvolatile Products, grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Be((CH_3)_2), 9.99</td>
<td>9</td>
<td>4.62, trace</td>
<td>0.35</td>
</tr>
<tr>
<td>2</td>
<td>Be((CH_3)_2), 9.15</td>
<td>9</td>
<td>2.50</td>
<td>3.35</td>
</tr>
<tr>
<td>3</td>
<td>Be((CH_3)_2), 9.90</td>
<td>9</td>
<td>3.37</td>
<td>3.94</td>
</tr>
<tr>
<td>4</td>
<td>Be((CH_3)_2), 18.1</td>
<td>12</td>
<td>2.35</td>
<td>0.91</td>
</tr>
<tr>
<td>5</td>
<td>Be((CH_3)_2), 19.0</td>
<td>12</td>
<td>2.38</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 13

SUMMARY OF \( \text{B}_4\text{H}_{10}/\text{B}_2\text{H}_6/\text{Be(CH}_3)_2 \) REACTIONS

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Reactants, mmoles</th>
<th>Reaction Time, hours</th>
<th>Volatile Products, mmoles</th>
<th>Nonvolatile Products, grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{Be(CH}_3)_2, 3.87 )</td>
<td>8</td>
<td>( \text{H}_2 ) 0.12 ( \text{B}_2\text{H}_6 ) 0.14 ( \text{B}<em>4\text{H}</em>{10} ) 3.06 ( \text{B(CH}_3)_3/3 ) 0.70 ( \text{CH}_3\text{BeBH}_4 ) 2 0.40</td>
<td>Liquid, 0.1191</td>
</tr>
<tr>
<td></td>
<td>( \text{B}<em>4\text{H}</em>{10}, 3.72 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( \text{Be(CH}_3)_2, 4.03 )</td>
<td>7.5</td>
<td>Neither measured nor identified</td>
<td>Liquid, 0.1222</td>
</tr>
<tr>
<td></td>
<td>( \text{B}<em>4\text{H}</em>{10}, 4.27 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{B}_2\text{H}_6, 1.25 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( \text{Be(CH}_3)_2, 4.81 )</td>
<td>15.3</td>
<td>( \text{H}_2 ) 0.39 ( \text{B}_2\text{H}_6 ) 3.89 ( \text{B}<em>4\text{H}</em>{10} ) 1.17 ( \text{CH}_3\text{BeBH}_4 ) 2 0.88</td>
<td>Liquid, 0.20</td>
</tr>
<tr>
<td></td>
<td>( \text{B}<em>4\text{H}</em>{10}, 4.89 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{B}_2\text{H}_6, 1.25 )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
estimated by material balance. The formulas derived for these materials were $\text{B}_3\text{H}_7(\text{CH}_3\text{BeH})_2\text{BH}_3(\text{experiment No. 1})$ and $\text{B}_3\text{H}_7(\text{Be}(\text{CH}_3)_2)_2$ ($\text{CH}_3\text{BeH})_2\text{BH}_3(\text{experiment No. 2})$.

(C) Analysis of Liquid Product, Experiment 2. The liquid product was analyzed by use of the sequential HCl/propionic acid procedure. The amounts of each constituent found and those calculated for a 39:61 mixture of $\text{B}_3\text{H}_7(\text{CH}_3\text{BeH})_2\text{Be}(\text{CH}_3)_2\text{BH}_3$ and $\text{B}_3\text{H}_7(\text{CH}_3\text{BeH})_2\text{BH}_3\text{CH}_3$ (0.0266-gram sample) were as follows. Found were: Be, 0.57 atom; B, 0.63 atom; H$_2$, 2.25 moles; CH$_4$, 0.62 mole; and B-alkyl CH$_3$, 0.10 mole. Calculated were: Be, 0.61 atom; B, 0.68 atom; H$_2$, 2.30 moles; CH$_4$, 0.68 mole; and B-alkyl CH$_3$, 0.10 mole.

Be(C$_2$H$_5$)$_3$ Reaction

(C) Be(C$_2$H$_5$)$_3$ (0.841 gram, 12.5 mmol) was treated with $\text{B}_4\text{H}_{10}$ (6.9 mmol) at ambient temperature. After 18 hours, a solid-liquid mixture had formed in the reactor. Approximately 24 hours after initiation of the reaction, the mixture reverted to a clear liquid. The reactor was opened and hydrogen (2.05 mmol) was removed. The volatile products were then removed and identified as being primarily $[(\text{C}_2\text{H}_5)\text{BH}]_2$ (0.305 gram; vapor pressure. 3 mm Hg at 0 C). The nonvolatile material consisted of a very thick liquid which was extracted with n-hexane. This treatment resulted in the separation of the viscous material into an insoluble solid and an n-hexane soluble product. Concentration of the n-hexane afforded the isolation of the liquid product $\text{B}_3\text{H}_7(\text{C}_2\text{H}_5\text{BeH})\text{BeH}_2\text{BH}_3$.

(C) Analyses for $\text{B}_3\text{H}_7(\text{C}_2\text{H}_5\text{BeH})\text{BeH}_2\text{BH}_3$ (0.0350-gram sample) were as follows. Calculated (in mmol) were: Be, 0.68; B, 1.35; hydridic hydrogen, 4.73; and hydrolyzable C$_2$H$_5$ groups, 0.34. Found were: Be, 0.63; B, 1.38; hydridic hydrogen, 4.42; and hydrolyzable C$_2$H$_5$ groups, 0.30.

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Be(C₂H₅)₂/B₂H₆ Reaction

(C) The first reaction was carried out by condensing B₂H₆ (4.08 mmoles) into a reactor containing the diethyl beryllium (0.3400 gram, 5.1 mmoles). After 15.5 hours at ambient temperature, the reaction products consisted of a solid-liquid mixture. Removal and fractionation of the volatile materials yielded (C₂H₅)_2B₂H₄ (1.68 mmoles), B(C₂H₅)₃ (0.72 mmole, and Be(NE₅)₂ (1.87 mmoles). A sample (0.0270 gram) of the nonvolatile solid recovered (0.1946) when hydrolyzed yielded H₂ (1.23 mmoles), C₂H₆ (0.01 mmole), Be(0.50 matom, and B (0.18 matom), indicating that the solid was essentially (BeH₂)_6[B(C₂H₅)₂]₂.

(C) The second reaction utilized a larger Be(C₂H₅)₂/B₂H₆ mole ratio (3.78/1.42). The reaction was halted after 18 hours. The reaction products were B(C₂H₅)_3 (1.74 mmoles), Be(NE₅)₂ (0.33 mmole), and a nonvolatile solid (0.0894 gram). A sample (0.0224 gram) of the nonvolatile solid when hydrolyzed yielded H₂ (1.69 mmoles), C₂H₆ (0.06 mmole), Be (0.71 matom), and B (0.16 matom) indicating again the formation of a boron alkyl-terminated beryllium hydride.

Be(NE₅)₂/Be(C₂H₅)₂ Reaction

(C) Beryllium borohydride (1.382 grams, 35.8 mmoles) was added to a reactor containing Be(C₂H₅)₂ (2.954 grams, 44.0 mmoles). The mixture became homogeneous after 0.5 hour at ambient temperature. Continued mixing resulted in the formation of a solid-liquid mixture from which B(C₂H₅)_3 (amount not measured) and an unknown were distilled. Isolation of the unknown from B(C₂H₅)_3 was accomplished by fractional condensation at 11, -45, and -196 °C; the unknown was retained by the -45 °C cooled trap. The liquid exhibited a vapor pressure of 2 mm Hg at 25 °C and analyzed as C₂H₅BH₂BeH₂(C₂H₅BeH)BH₃. Found (0.0793 gram sample) in mmoles were: Be, 1.50; B, 1.45; hydridic hydrogen, 6.0; and hydrolyzable C₂H₅ groups, 0.82. Calculated in mmoles were: Be, 1.50; B, 1.50; hydridic hydrogen, 6.0; and hydrolyzable C₂H₅ groups 0.75.
Reaction of $\text{Be(C}_2\text{H}_5)_2$ and Tetraethyl diborane

(C) **Simple Mixing.** A 2:1 mixture of the reactants was prepared by condensing at -196°C, tetraethyl diborane (0.2985 gram, admixed with 5 weight percent of triethyl diborane by analysis) into a tube reactor containing the beryllium alkyl (1.06 mmoles). The mixture was then warmed to ambient temperature while stirring. After equilibrating the mixture for 72 hours, the entire sample was hydrolyzed. Mass spectrometric analyses of the gases collected (4.56 mmoles) indicated the composition to be 99.9 mole percent $\text{H}_2$ and 0.1 mole percent $\text{C}_2\text{H}_6$. The quantity of hydrogen collected was in agreement with that expected (4.45 mmoles) based on analysis of the tetraethyl diborane. The absence of ethane in any appreciable quantities illustrated the near-quantitative hydriding of the beryllium.

(C) **Attempted Isolation of $\text{BeH}_2[\text{BH(C}_2\text{H}_5)_2]_2$.** An aliquot of the tetraethyl diborane (0.4803 gram) used previously and $\text{Be(C}_2\text{H}_5)_2$ (1.71 mmoles) were mixed in the manner described above. The reactor containing a clear liquid was cooled to 0°C after a reaction time of 72 hours at ambient temperature. The materials volatile at 0°C were removed from the reactor during 9 hours leaving a clear glass. The entire volatile (0.5411 gram) and nonvolatile (0.0540 gram) fractions were separately hydrolyzed to yield the following results. The volatile fraction contained: Be, 0.79 matom; B, 7.37 matoms; hydridic hydrogen, 4.62 mmoles; and hydrolyzable $\text{C}_2\text{H}_5$ groups, 0.38 mmole. The nonvolatile fraction contained: Be, 0.79 matom; B, 0.23 matom; hydridic hydrogen, 2.44 mmoles; and hydrolyzable $\text{C}_2\text{H}_5$ groups, 0.09 mmole.

(C) **A third experiment in which $\text{Be(C}_2\text{H}_5)_2$ (1.65 mmoles) was added in the liquid state to $[\text{BH(C}_2\text{H}_5)_2]_2$ (0.4900 gram), maintained at ambient temperature, yielded similar results.** The volatile (0.5400 gram) and nonvolatile (0.1385 gram) fractions were separated as during the preceding experiment. Hydrolysis of the entire samples and analyses of the hydrolysate yielded the following results. Volatile fraction: Be, 0.80 matom; B, 7.01 matoms; hydridic hydrogen, 5.86 mmoles; hydrolyzable $\text{C}_2\text{H}_5$ groups, 0.06 mmole;
nonvolatile fraction: Be, 0.65 matom; B, 0.48 matom; hydridic hydrogen, 2.22 moles; hydrolyzable \( \text{C}_2\text{H}_5 \) groups, 0.01 mole.

\[
\text{B}_4\text{H}_{10}/[(\text{C}_2\text{H}_5)_2\text{Be}\cdot\text{C}_2\text{H}_5\text{BeH}]_x \text{ Reaction}
\]

(C) The copolymer \([(\text{C}_2\text{H}_5)_2\text{Be}\cdot\text{C}_2\text{H}_5\text{BeH}]_x \) (0.7369 gram, 7.50 matoms of Be) was treated with \( \text{B}_4\text{H}_{10} \) (4.82 moles) for 94 hours. The volatile products were \( \text{H}_2 \) (1.43 moles) and \( \text{B}(\text{C}_2\text{H}_5)_3 \) (2.31 moles); \( \text{B}_4\text{H}_{10} \) (0.53 mole) was also recovered. The nonvolatile liquid product was treated with an additional quantity of \( \text{B}_4\text{H}_{10} \) (1.54 moles) for 23 hours, after which time \( \text{H}_2 \) (0.23 mole), \( \text{B}_4\text{H}_{10} \) (0.70 mole) and \( \text{B}(\text{C}_2\text{H}_5)_3 \) (0.32 mole) were recovered. The nonvolatile liquid product, containing a small amount of suspended solid, was extracted with n-hexane, filtered, and the n-hexane filtrate concentrated. The amount of liquid recovered was 0.5338 gram.

(C) Analysis of a sample (0.0352 gram) of the liquid yielded \( \text{H}_2 \) (2.85 moles), \( \text{B} \) (0.0085 gram, 0.79 matom), Be (0.0061 gram, 0.68 matom), and hydrolyzable \( \text{C}_2\text{H}_5 \) groups, as ethane, (0.54 mole). This results in Be:B:H: \( \text{C}_2\text{H}_5 \) ratios of 5.0:5.8:21.0:4.0; calculated for \( \text{(B}_3\text{H}_4\text{)}_2\text{(C}_2\text{H}_5\text{BeH})_4\text{BeH}_2 \) are: 5:6:22:4.

\[
\text{B}_4\text{H}_{10}/\text{B}_2\text{H}_6/[(\text{C}_2\text{H}_5)_2\text{Be}\cdot\text{C}_2\text{H}_5\text{BeH}]_x \text{ Reaction}
\]

(C) Treatment of a \([(\text{C}_2\text{H}_5)_2\text{Be}\cdot\text{C}_2\text{H}_5\text{BeH}]_x \) sample (0.6707 gram, 12.2 matoms of Be) with a mixture of \( \text{B}_4\text{H}_{10} \) (5.31 moles) and \( \text{B}_2\text{H}_6 \) (1.45 moles) resulted in liquefaction of the copolymer in less than 48 hours. The volatile products were \( \text{H}_2 \) (1.42 moles) and \( \text{B}(\text{C}_2\text{H}_5)_3 \) (3.08 moles); \( \text{B}_4\text{H}_{10} \) (1.07 moles) was also recovered. The liquid product when extracted with n-hexane precipitated a quantity of solid. The filtrate after concentration yielded a clear mobile liquid weighing 0.1253 gram.

(C) Analysis of a sample (0.0214 gram) of the liquid yielded \( \text{H}_2 \) (1.95 moles), \( \text{B} \) (0.0064 gram, 0.59 matom), Be (0.0034 gram, 0.38 matom), and hydrolyzable
groups, as ethane, (0.29 mmole). This results in Be:B:H:C ratios of 3.93:6.09:20.2:3.00; calculated for \((B_3H_7)_2(C_2H_5BeH)_3\) are: 3:6:21:3.

\[ C_2H_5BeH/B_4H_{10} \text{ Reaction} \]

(C) A toluene solution of \((C_2H_5BeH)_x\) was prepared by reacting \((BeH_2)_x[B(C_2H_5)_3]_2\) (0.189 gram, 11 mmoles of \(BeH_2\)) with \(Be(C_2H_5)_2\) (0.752 gram, 11.2 mmoles) in \(CaH_2\)-dried toluene (25 milliliters) at 50°C. After 72 hours, the small amount of remaining insoluble material was removed by filtration. A 2-milliliter aliquot of the filtrate was hydrolyzed yielding \(H_2\) (2.41 mmoles), \(C_2H_5\) (2.55 mmoles), and \(Be\) (22.9 mg, 0.254 mmole). The concentration of \((C_2H_5BeH)_x\) in toluene (1.2 mmoles/milliliter) was calculated from these data.

(C) \(B_4H_{10}\) (1.74 mmoles) was added to an aliquot of the toluene solution (4 milliliters, 4.8 mmoles of \(C_2H_5BeH\)). An immediate reaction occurred between the two reagents resulting in the deposition of solids. Filtration and concentration of the filtrate by vacuum distillation at ambient temperature resulted in no nonvolatile liquid products.

\[ B_4H_{10}/B_2H_6/(CH_3BeH)_x \text{ Reaction} \]

(C) The \((CH_3BeH)_x\) used during this experiment was prepared from \(Be(CH_3)_2\) and metathetical \((BeH_2)_x\) (Ref. 8). End group analyses (boron analyses) of the synthesized alkylberyllium hydride, coupled with those for \(Be\), hydridic hydrogen, and hydrolyzable \(CH_3\) (measured as \(CH_4\)), indicated the composition \([CH_3BeH]_2[Be(CH_3)_2]_2[B(C_2H_5)_3]\).

(C) A sample of the preceding compound (0.3858 gram, 11.0 mmoles of \(Be\)) was treated with a mixture of \(B_4H_{10}\) (5.15 mmoles) and \(B_2H_6\) (2.20 mmoles). During 3 hours at ambient temperature, the glassy alkylberyllium hydride was converted to a mobile liquid. Materials volatile at ambient temperature were \(H_2\) (0.11 mmole), \(B_2H_6\) (0.01 mmole), \(B(CH_3)_3\) (0.16 mmole), unreacted \(B_4H_{10}\) (4.8 mmoles), and \((CH_3BeH)_2\) (2.01 mmoles).
(c) The residual liquid was analysed using the sequential HCl/propionic acid procedure. The amounts of each constituent found and those values calculated for a 48:50 mixture (0.0277 gram sample) of $\text{BeH}_2(\text{CH}_3\text{BeH})_5(\text{Be}(\text{CH}_3)_2)$-$\text{BeH}_7$ and $\text{BeH}_2(\text{CH}_3\text{BeH})_6[\text{Be}(\text{CH}_3)_2]\text{BH}_2(\text{CH}_3)_2$ were as follows. Found were: Be, 0.68 mole; B, 0.42 mole; H, 1.87 moles; CH$_4$, 0.79 mole; and B-alkyl CH$_4$, 0.11 mole. Calculated were: Be, 0.68 mole; B, 0.42 mole; H, 1.86 moles; CH$_4$, 0.78 mole; and B-alkyl CH$_4$, 0.11 mole.

(c) A sample of the above liquid mixture (0.0528 gram) was treated with additional B$_4$H$_{10}$ (1.16 moles) and B$_2$H$_6$ (0.12 mole) at ambient temperature for 2.5 hours. The excess boranes and volatile products were removed but not identified. Analyses of the residual liquid (sample size, 0.0262 gram), using aqueous HCl only, satisfied the composition $\text{BeH}_2(\text{CH}_3\text{BeH})_6\text{BH}_2\text{CH}_3$. Found were: Be, 0.70 mole; B, 0.46 mole; H, 1.86 moles; and CH$_4$, 0.71 mole. Calculated were: Be, 0.69 mole; B, 0.46 mole; H, 1.85 moles; and CH$_4$, 0.71 mole.

$\text{B}_4\text{H}_{10}/(\text{BeH}_2)_x$ Reaction

(c) Tetraborane (4.95 mmoles) was added to a reactor containing boron alkyl-terminated $\text{BeH}_2$ (0.0785 gram, 65.1 percent purity, 4.6 mmoles of $\text{BeH}_2$). After a reaction time of 4 days, hydrogen (2.45 mmoles), unreacted $\text{B}_4\text{H}_{10}$ (1.80 mmoles), $\text{B}_2\text{H}_6$ (0.09 mmole), $\text{Be}(\text{BH}_4)_2$ (0.0347 gram, 0.9 mmole), and trace amounts of ethyldiboranes were recovered.

1,2-Trimethylenediborane/$\text{BeH}_2$ Reaction

(u) The preparation of 1,2-trimethylenediborane was carried out according to the procedure of Lindner and Onak (Ref. 12). The vapor-phase hydroboration of allene was performed in a circulating system (3.5-liter volume) containing C$_2$H$_6$ (64 millimeters), $\text{B}_2$H$_6$ (181 millimeters), and He (275 millimeters). The mixture was circulated through a heated (92 to 93°C) reaction zone until the total pressure in the system reached a constant value. The reaction products were continuously trapped at -78°C, and the diborane...
derivative separated from the excess $\text{B}_2\text{H}_6$ by fractional condensation at -97 C. Infrared and hydrolytic analyses of the product indicated a mixture of 1,2-trimethylenediborane (70 percent) and n-propyldiborane (30 percent). This mixture was used without further purification.

(C) An analyzed sample of \((\text{BeH}_2)_x(\text{BH}_3)_2\) (0.0612 gram, 4.0 moles of BeH$_2$) was treated at ambient temperature with the impure 1,2-trimethylenediborane (0.3076 gram, 3.15 moles). No apparent reaction occurred after 16 hours under these conditions. After 4 hours at 57 C, clumps of colorless needles, Be(BH$_4$)$_2$, formed above the hot zone. The total amount of volatile products weighed 0.0829 gram but were not further investigated because the nonvolatile product was a pasty solid.

PREPARATION OF ATBH LIQUIDS

Reaction of Beane With $\text{Al(CH}_3\text{)}_3$

(C) The reactivity of Beane with $\text{Al(CH}_3\text{)}_3$ at 130 C as a function of time was determined in the following manner. Six ampoules containing weighed amounts of Beane (96-percent purity) and commercial grade $\text{Al(CH}_3\text{)}_3$ were sealed off in vacuo, and tumbled in an oil bath maintained at 130 C. After a specified time, the ampoule was removed from the oil bath, the ampoule was opened, and the unreacted Beane collected by filtration and carefully washed with n-hexane. After drying in vacuo, the weight of Beane recovered gave a measure of the extent of reaction with $\text{Al(CH}_3\text{)}_3$ (Table 14).

(C) The insoluble solid, remaining from the $\text{Al(CH}_3\text{)}_3$/Beane reaction, was identified in the following manner. A mixture of Beane (0.50 gram) and $\text{Al(CH}_3\text{)}_3$ (10 milliliters) was heated, while stirring, at 120 C for 16 hours. The mixture was pressure filtered, and the solid was washed well with n-hexane. A sample (0.0203 gram) of the insoluble material recovered (0.2543 gram) was then analyzed for beryllium (1.69 atoms), hydridic hydrogen (5.80 moles) and aluminum (< 0.1 mg). The recovered Beane, based on the beryllium result, was 92 percent pure.

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TABLE 14

REACTION OF BEANE AND Al(CH$_3$)$_3$ AT 130 C

<table>
<thead>
<tr>
<th>Heating Time, hours</th>
<th>Beane Used, milligrams*</th>
<th>Al(CH$_3$)$_3$ Used, milligrams</th>
<th>Beane Recovered, milligrams</th>
<th>Beane Reacted, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>50.9</td>
<td>638.8</td>
<td>17.8</td>
<td>67.7</td>
</tr>
<tr>
<td>16</td>
<td>54.6</td>
<td>677.5</td>
<td>13.0</td>
<td>79.4</td>
</tr>
<tr>
<td>24</td>
<td>59.9</td>
<td>637.8</td>
<td>9.8</td>
<td>84.0</td>
</tr>
<tr>
<td>48</td>
<td>55.7</td>
<td>680.4</td>
<td>3.0</td>
<td>98.6</td>
</tr>
<tr>
<td>72</td>
<td>55.2</td>
<td>685.2</td>
<td>2.4</td>
<td>99.7</td>
</tr>
</tbody>
</table>

*Purity of Beane, 96 weight percent

Composition of ATBH Liquid vs Reaction Time

(C) The n-hexane extracts from the preceding experiments were subjected to vacuum pumping until the loss in weight per hour was 2 to 3 milligrams. This resulted in the removal of the n-hexane as well as any unreacted Al(CH$_3$)$_3$. The analytical results obtained on the nonvolatile materials are presented in Table 15.

TABLE 15

ANALYSES OF Al(CH$_3$)$_3$/BEANE PRODUCTS

<table>
<thead>
<tr>
<th>Heating Time, hours</th>
<th>Weight of Product, milligrams</th>
<th>Analyses, mole ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>8</td>
<td>113.7</td>
<td>2</td>
</tr>
<tr>
<td>16</td>
<td>131.8</td>
<td>2</td>
</tr>
<tr>
<td>24</td>
<td>160.1</td>
<td>2</td>
</tr>
<tr>
<td>48</td>
<td>152.7</td>
<td>2</td>
</tr>
<tr>
<td>72</td>
<td>168.5</td>
<td>2</td>
</tr>
</tbody>
</table>

A trend toward decreased methyl group and increased hydride contents with longer reaction time is indicated from these data.
Formation of Dimethylalane

(C) The formation of dimethylalane as a byproduct of the Al(CH$_3$)$_3$/Beane system was investigated as follows. A mixture of Beane (0.033 gram, 96 percent purity, 2.9 mmoles) and commercial grade Al(CH$_3$)$_3$ (0.350 gram, 4.9 mmoles) was heated for 24 hours at 120°C. The volatile materials (0.310 gram) were then removed by vacuum pumping. Analyses of the volatile materials in toto revealed Be:Al:CH$_3$:H mole ratios of 1:20.9:59.7:8.1. These results agree favorably with those expected based on a mixture of Al(CH$_3$)$_3$ (64.5 percent), (CH$_3$)$_2$AlH (33.5 percent), and CH$_3$BeH (2.0 percent) present in the form of a complex with either or both of the alanes.

Reaction of Beane and Dimethylalane

(C) A mixture of Beane (0.0522 gram, 96 weight percent BeH$_2$, 4.55 mmoles) and dimethylalane (0.595 gram, containing 12 weight percent monomethylalane by analysis) was heated at 130°C for 24 hours. The mixture was then processed in the same manner used for the Al(CH$_3$)$_3$ studies. Analysis of the filtrate showed the presence of 21.3 percent of the beryllium used. The liquid nonvolatile product (0.2075 gram) was quite viscous and had the Al/Be/H/CH$_3$ ratios of 2.0/0.68/2.99/4.08, indicating the presence of residual dimethylalane.

Hydriding of ATBH Liquids

(C) A mixture of Al(CH$_3$)$_3$ (104 mmoles) and Beane (45.4 mmoles) was heated at 120°C for 16 hours. The filtered solution was used as the standard ATBH liquid for the hydriding reactions. An aliquot (2 milliliters) of the filtrate was taken and the excess Al(CH$_3$)$_3$ was removed until constant weight (0.120 ±0.002 gram) was achieved. Analysis of the viscous residue gave the Be:H:CH$_3$ ratio of 1.0:1.0:1.85.
(C) B₂H₆ Reaction. A 2-milliliter aliquot of the standard ATEH material was pumped to constant weight (0.1185 gram) and subsequently treated with B₂H₆ (0.455 mmole) at ambient temperature. The mixture became quite mobile within a few minutes after reaching ambient temperatures. The volatile components (0.0588 gram) were fractionated to obtain B(CH₃)₃ (0.06 mmole) and an aluminum-containing liquid. Analysis of the nonvolatile viscous material revealed the Be:H:CH₃ ratio of 1:1.5:0.93. The amount of aluminum (14.9 milligrams) found in the volatile fraction corresponded to a 80 percent displacement.

(C) Be(BH₄)₂ Reaction. A sample (0.1204 gram) of the ATEH material, as obtained above for the previous reaction, was treated with Be(BH₄)₂ (0.0175 gram, 0.452 mmole) at ambient temperature. The viscous ATEH material became quite mobile and contained only a small quantity of solid after 1 hour; all but a trace of this material dissolved after stirring overnight. Fractional condensation yielded an aluminum-containing compound but no alkyl-boron derivatives. Analyses of the nonvolatile viscous material revealed the Be:H:CH₃ ratio of 1:1.8:0.92, while the volatile fraction contained 82 percent of the aluminum.

(C) B₄H₁₀ Reaction. A third sample (0.1213 gram) of the prepared ATEH liquid was treated with B₄H₁₀ (0.429 mmole) at ambient temperature. The liquid required approximately 1 hour to become mobile. After stirring the mixture for 16 hours, the liquid products were separated into volatile and nonvolatile fractions which were subsequently analyzed. The volatile portion contained approximately 85 percent of the aluminum while the nonvolatile liquid material had Be:H:CH₃ ratios of 1.0:2.9:1.0.

Decomposition of Be(C₂H₅)₂ at Ambient Temperature

(U) The precipitate formed during ambient temperature storage of Be(C₂H₅)₂ was triturated under n-hexane, filtered, and washed copiously with the same hydrocarbon. The solid was then dried in vacuo for 30 minutes.
Analysis of a sample (0.0562 gram) of the solid revealed $H_2(0.53$ mmole), hydrolyzable $C_2H_5$ groups (1.59 mmoles), and Be (1.0 matom). This resulted in $Be:C_2H_5:H$ ratios of 1.9:3.0:1.0; calculated for the monomeric unit $(C_2H_5)_2Be·C_2H_5BeH$ were: 2:3:1.

Pyrolysis of $Be(C_2H_5)_2$

(U) In an attempt to prepare samples of the purported compound $C(BeH_2BeC_2H_5)_4$ from the pyrolysis of $Be(C_2H_5)_2$, several runs were made at 200 C for varying time periods. A typical pyrolysis was conducted in the following manner to yield the indicated volatile species. A sample of $Be(C_2H_5)_2$ (4.26 grams, 63.5 mmoles) was heated in a sealed flask for 1.5-hour intervals at temperatures up to 200 C for a total time of 16 hours. After this time period, the evolution of pyrolysis gases had ceased. The volatile products consisted of $H_2 (0.25$ mmole), $C_2H_6 (19.6$ mmoles), $C_2H_4 (1.2$ mmoles), and 0.629 gram of a mixture of higher hydrocarbons; the higher hydrocarbons were identified by mass spectrometric analyses as propene, n-propane, 2-butene, n-butane, and pentanes.

(U) Analytical data obtained on the crude yellow product from two different runs are presented in Table 16.

**TABLE 16**

ANALYSES OF CRUDE PYROLYSIS PRODUCT OF $Be(C_2H_5)_2$

<table>
<thead>
<tr>
<th>Sample Size, mg</th>
<th>$H_2$, mmoles</th>
<th>$CH_4$, mmoles</th>
<th>$C_2H_6$, mmoles</th>
<th>Be, matoms</th>
<th>$Be:H:C_2H_6:CH_4$ Ratios</th>
<th>Material Balance, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>139.2</td>
<td>2.39</td>
<td>0.39</td>
<td>1.28</td>
<td>2.92</td>
<td>8.0:6.5:3.5:1.1</td>
<td>51.6</td>
</tr>
<tr>
<td>91.8</td>
<td>1.50</td>
<td>0.22</td>
<td>0.82</td>
<td>1.68</td>
<td>8.0:7.1:3.9:1.1</td>
<td>47.7</td>
</tr>
</tbody>
</table>
Samples of the crude product were twice-distilled at 90 to 95 °C (5 x 10^{-4} \text{ mm Hg}) in a Hickman Molecular Still. Distillation did not yield a material of high purity. Analytical data for distilled samples are presented in Table 17.

**TABLE 17**

**ANALYSES OF DISTILLED PYROLYSIS PRODUCT OF \( \text{Be}(\text{C}_5\text{H}_5)^2 \)**

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Sample Size, ( \text{mg.} )</th>
<th>( \text{H}_2 ) mmoles</th>
<th>( \text{CH}_4 ) mmoles</th>
<th>( \text{C}_2\text{H}_6 ) mmoles</th>
<th>Be, matoms</th>
<th>( \text{Be} : \text{H} : \text{C}_2\text{H}_6 : \text{CH}_4 ) Ratios</th>
<th>Material Balance Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>66.3</td>
<td>1.58</td>
<td>0.22</td>
<td>0.84</td>
<td>1.54</td>
<td>8.0:8.2:4.4:1.1</td>
<td>65.1</td>
</tr>
<tr>
<td>2</td>
<td>51.7</td>
<td>1.09</td>
<td>0.26</td>
<td>0.98</td>
<td>1.31</td>
<td>8.0:6.7:6.0:1.4</td>
<td>87.6</td>
</tr>
<tr>
<td>3</td>
<td>60.6</td>
<td>1.52</td>
<td>0.23</td>
<td>0.77</td>
<td>1.55</td>
<td>8.0:7.9:4.0:1.2</td>
<td>68.2</td>
</tr>
</tbody>
</table>

A separate sample of the liquid from experiment No. 1 was treated with D_2O to determine if the diluent was chemically or physically bound in the mixture. After deuterolysis, the hydrolyzate was extracted with n-pentane, the n-pentane was removed, and the residual oil was examined by infrared spectroscopy for C-D absorptions. No absorptions attributable to C-D bonds were found.
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INVESTIGATION OF LIQUID-METAL HYDRIDES

ABSTRACT

Studies of liquid beryllium hydride synthesis have resulted in a number of new species with theoretical specific impulses approaching 330 seconds and further defined the most promising classes of this type of high-energy fuel. In general, it appears that terminators derived from higher borane fragments (e.g., B_3H_7) are more advantageous than simple BH_3 terminators. Liquids with B_3H_7 terminators exhibit high theoretical impulse and satisfactory fluidity, and unlike many BH_3-terminated liquids, are not subject to reversible dissociation. The bulk of this investigation was concerned with the preparation of borane-terminated beryllium hydride (BTBH) liquids from the reaction of B_4H_{10} with beryllium alkyls and alkylberyllium hydrides. The nature of the reaction products was dependent upon the experimental conditions. The use of a B_4H_{10}/Be(CH_3)_2 mole ratio of 0.5 and an extended reaction time yielded the best product, a liquid analyzing as B_7H_2(CH_3BeH)_2BeH_2BH_3 (specific impulse, 329 seconds with H_2O_2). The use of B_6H_6/B_4H_{10} mixtures simplified the complex reactions involving pure B_4H_{10} and solid beryllium compounds. Such mixtures increased the liquefaction rates of the beryllium compounds and also resulted in a significant decrease in the amount of B_4H_{10} decomposition during its reactions. Ethyl-substituted BTBH liquids were synthesized. The compound B_7H_2(CH_3BeH)_2BeH_2BH_3 (specific impulse, 326 seconds) remained fluid at -40°C. Conditions for the quantitative reaction of Al(CH_3)_3 and Beane were established for the preparation of alane-terminated beryllium hydride (ATBH) liquids. The displacement of the alane terminators from ATBH liquids by B_6H_6, B_4H_{10}, or Be(BH_4)_2 demonstrated the feasibility of employing ATBH materials as precursors for BTBH liquids.
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