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(Unclassified Title)

FINAL REPORT,
INVESTIGATION OF LIQUID-METAL HYDRIDES

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

TECHNICAL REPORT AFRPL-TR-67-134

April 1967

Group 4
Downgraded at 3-Year Intervals
Declassified After 12 Years

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Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards, California 93523
Air Force Systems Command
United States Air Force

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CONFIDENTIAL ABSTRACT

(C) 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.

(C) 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 $B_3H_7(CH_3BeH)_2BeH_2BH_3$ (specific impulse, 329 seconds with H_2O_2).

(C) The use of B_2H_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.

(C) Ethyl-substituted BTBH liquids were synthesized. The compound $B_3H_7 - (C_2H_5BeH)BeH_2BH_3$ (specific impulse, 326 seconds) remained fluid at -40 C.

(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_2H_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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INTRODUCTION

(C) 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 H_2O_2 as the oxidizer, a great deal of interest has been generated in attempting to develop related storable liquid propellant systems.

(C) 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.

(C) 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 B_4H_{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 B_3H_7 - $(CH_3BeH)_2BeH_2BH_3$ (specific impulse, 329 seconds).

(C) 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 B_3H_7, leads to good

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fluidity and high specific impulse, but that further increases in BeH_2 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 BTBH Fuels. Because of the interrelationship of the work performed under these phases, the results are reported in a combined fashion.

PERFORMANCE OF LIQUID BERYLLIUM FUELS

(C) The theoretical specific impulse values of some postulated liquid beryl-
lium fuels are compared with that of BeH_2 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 BTBH liquids are listed,
and both borane (BH_3) and triborane (B_3H_7) terminators or their alkyl de-
rivatives 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 BH_3 group than in the B_3H_7 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

Compound	Estimated Heat of Formation, kcal/mole	Specific Impulse with H_2O_2 (shifting, 1000 → 14.7 psia), seconds
$(BeH_2)_n$	-5.6	357
$H_3B(CH_3BeH)(BeH_2)_9BH_3$	-82	352
$H_3B(CH_3BeH)(BeH_2)_3BH_3$	-45 (-11)	342 (351)
$H_3B(BeH_2)_2(CH_3BeH)_2BH_3$	-47 (-12)	338 (341)
$(CH_3BH_2)_2(BeH_2)_4$	-70 (-37)	333 (336)
$H_3B(C_2H_5BeH)_3(BeH_2)_6BH_3$	-85	333

TABLE 2

THEORETICAL PERFORMANCE OF SOME KNOWN

BERYLLIUM LIQUIDS

Compound	Estimated Heat of Formation, kcal/mole	Specific Impulse With H_2O_2 (shifting $1000 \rightarrow 14.7$ psia), seconds
$B_3H_7(CH_3BeH)_2(BeH_2)BH_3$	-20	329
$B_3H_7(CH_3BeH)_3(BeH_2)BH_3$	-50	326
$B_3H_7(C_2H_5BeH)(BeH_2)BH_3$	-10	326
$B_3H_7(CH_3BeH)_2BH_3$	-15	320
$C_2H_5BH_2(C_2H_5BeH)(BeH_2)BH_3$	-20	311
$(B_3H_7)_2(C_2H_5BeH)_4(BeH_2)$	-20	315
$(B_3H_7)_2(C_2H_5BeH)_3(BeH_2)$	-10	317
$(CH_3B_3H_6)_2(CH_3BeH)_3(BeH_2)$	-35	321

DISCUSSION AND RESULTS

PREPARATION OF THE BTBH LIQUIDS

(C) 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

Beryllium Compounds	Borane Agents	Beryllium-Boron Agents
$[(CH_3)_2Be]_n$	B_4H_{10}	$Be(BH_4)_2$
$[(C_2H_5)_2Be]_n$	B_2H_6	$(CH_3BeBH_4)_2$
$[(C_2H_5)_2Be \cdot C_2H_5BeH]_n$	alkyldiboranes	
$[CH_3BeH]_n$		
$(BeH_2)_n$		

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.

(C) The simplest of the BTBH liquids to prepare are those involving dimethyl-beryllium and $Be(BH_4)_2$ or $(CH_3BeBH_4)_2$. 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 $(CH_3B_3H_6)_2(CH_3BeH)_3BeH_2$, however, was much more stable, even though a $B-CH_3$ bond was already present in the material. On this basis, B_3H_7 termination appeared to be a logical approach to the preparation of thermally stable BTBH liquids.

(U) A summary of the B_4H_{10} reactions investigated is presented in Table 4. A more detailed description of the reactions is presented in the following paragraphs.

$B_4H_{10}/Be(CH_3)_2$ Reaction System

(C) The reaction of B_4H_{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 ≥ 330 seconds.

1. Relationship of the physical state of B_4H_{10} to its reactivity

2. Mole ratios of the reactants

3. Reaction time

4. Effect of B_2H_6 as an initiating agent for $Be(CH_3)_2$ liquefaction

Throughout these studies, temperatures were maintained at ambient or below to hold the decomposition of B_4H_{10} (one of the unstable boranes) to a minimum. However, such decomposition was not completely avoidable.

TABLE 4

SUMMARY OF B_4H_{10}/Be(CH$_3$)$_2$ REACTIONS

Experiment No.	B_4H_{10}/Be(CH$_3$)$_2$ Mole Ratio	Reaction Conditions	Comments
1	1.0	Liquid B_4H_{10} at ambient temperature	No significant amounts of liquid beryllium products were formed. The principal beryllium-containing product was BeH_2.
2	1.0	B_4H_{10} vapor at ambient temperature	Liquefaction of the Be(CH$_3$)$_2$ occurred after 26 hours. The liquid analyzed as $[(CH_3)_3B_3H_4]_2(BeH_2)_2(CH_3BeH)_2$.
3	2.0	B_4H_{10} vapor at ambient temperature	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.
4	1.0	B_4H_{10} vapor at ambient temperature	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.
5	0.5	B_4H_{10} added incrementally at ambient temperature	Conversion of the Be(CH$_3$)$_2$ to liquid products was complete after 120 hours. A liquid analyzing as $B_3H_7(CH_3BeH)_2BeH_2BH_3$ was isolated.
6	0.5	B_4H_{10} added incrementally at ambient temperature	After 120 hours, a liquid was isolated which analyzed as $B_3H_7(CH_3BeH)_2BH_2CH_3$.

(C) Physical State of B_4H_{10} and Its Reactivity. The products of the $\overline{Be(CH_3)_2/B_4H_{10}}$ reaction are quite dependent upon the physical state of the B_4H_{10}. The reaction of equimolar amounts of $Be(CH_3)_2$ and liquid B_4H_{10}, a condition under which hydriding of the beryllium alkyl was expected to be extensive, never yielded a one-phase system. Instead, the slurry of $Be(CH_3)_2$ and liquid B_4H_{10} 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 BeH_2.

(C) The reaction of equimolar amounts of $Be(CH_3)_2$ and B_4H_{10} 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 $[(CH_3)_3B_3H_4]_2 (CH_3BeH)_2(BeH_2)_2$ was a mobile liquid, but its high methyl group content negated its importance as a high-energy fuel.

(C) In the presence of liquid B_4H_{10}, the hydriding of $Be(CH_3)_2$ to BeH_2 is quite rapid. The failure to obtain appreciable quantities of BTBH liquids when liquid B_4H_{10} was used as the reactant was attributed to the more favorable formation of solid BeH_2 in this reaction medium. Under comparable experimental conditions, however, the B_4H_{10} vapor-phase reaction, being a solid/gas reaction, was a much slower reaction and the extent of hydriding of the $Be(CH_3)_2$ was much less. This reasoning is supported by the nature of the products obtained.

(C) Mole Ratios of B_4H_{10} and $Be(CH_3)_2$. Although low $B_4H_{10}/Be(CH_3)_2$ mole ratios would be expected to yield liquids with the higher degrees of polymerization, these conditions would also most likely result in slower $Be(CH_3)_2$ 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 B_4H_{10} (vapor)/$Be(CH_3)_2$ mole ratios of 0.5, 1.0, and 2.0 to determine the relative rates of $Be(CH_3)_2$ liquefaction (Table 4). The rate of conversion of $Be(CH_3)_2$ to liquid products decreased in the order 2.0 > 1.0 > 0.5. A consideration of the instability of B_4H_{10}, however, suggested that these same results could be explained by assuming that the $Be(CH_3)_2$ liquefaction was initiated by a disproportionation product of B_4H_{10}, most likely B_2H_6, rather than B_4H_{10} itself. Although the total amount of B_4H_{10} 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 B_4H_{10} vapor in contact with the $Be(CH_3)_2$ was identical at any given time. This was the case because the amount of B_4H_{10} vapor was governed by the vapor pressure of the liquid boron hydride present. The postulate that B_2H_6, derived from the disproportionation of B_4H_{10}, was initiating the liquefaction of $Be(CH_3)_2$ was tested experimentally.

(C) Influence of B_2H_6 on the B_4H_{10}/$Be(CH_3)_2$ Reaction. The reaction of $Be(CH_3)_2$ with mixtures of B_4H_{10} and B_2H_6 (mole ratio ~ 4:4:1, respectively) resulted in approximately a fourfold decrease in the time required (6 vs 26 hours) for liquefaction of the $Be(CH_3)_2$ by B_4H_{10} alone (Table 5). From earlier work on the B_2H_6/$Be(CH_3)_2$ system (Ref. 1), it is known that the amount of B_2H_6 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 B_2H_6 and B_4H_{10}. However, the liquids isolated from these reactions were found to contain significant amounts of methyl groups.

(C) Decomposition of B_4H_{10} During Reaction. The preceding discussion has demonstrated some of the difficulties associated with the use of B_4H_{10} as a liquefying agent for $Be(CH_3)_2$, viz:

1. Instability of B_4H_{10}
2. Slow reaction rates

TABLE 5

SUMMARY OF $B_4H_{10}/B_2H_6/Be(CH_3)_2$ REACTIONS

(Vapor-Phase Reaction at Ambient Temperature)

Experiment No.	$B_4H_{10}/B_2H_6/Be(CH_3)_2$ Mole Ratio	Comments
1	4.0:1.0:4.2	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 $B_3H_7(CH_3BeH)_2[(CH_3)_2Be]_3BH_3$.
2	4.0:1.0:3.8	Conversion of the $Be(CH_3)_2$ 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 $B_3H_7(CH_3BeH)_2[Be(CH_3)_2]BH_3$ and $B_3H_7(CH_3BeH)_4BH_2CH_3$.
3	3.9:1.0:3.8	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 $B_3H_7[Be(CH_3)_2]_2(CH_3BeH)_2BH_3$.

Disproportionation products of B_4H_{10} other than B_2H_6 are B_5H_9, B_5H_{11}, H_2, and nonvolatile $(BH)_x$ 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 B_2H_6 to increase the liquefaction rate of $Be(CH_3)_2$ also served to suppress the disproportionation of B_4H_{10}. For example, when the stability of a 1:4 mixture of B_2H_6 and B_4H_{10} was tested for 8 hours at ambient temperature, the B_4H_{10} was recovered quantitatively. The recovery of B_4H_{10} from this test was greater than predicted based upon the decomposition of B_4H_{10} vapor at low pressures (40 millimeters, Ref. 7). It was also observed that 31 percent of the B_2H_6 was not recovered from the stability experiment (conducted at a total pressure of approximately 650 millimeters). Conversion of the more stable boron hydride B_2H_6 to B_4H_{10}, a known reaction at much higher pressures, must have occurred to replenish any B_4H_{10} which disproportionated (Eq. 1).

$$2B_2H_6 \longrightarrow B_4H_{10} + H_2 \tag{1}$$

Evidence for this type of reaction was the correspondence of unrecovered B_2H_6 and the H_2 formed during the stability experiment.

(C) Reaction Time. As a result of the disproportionation of B_4H_{10}, the reaction time required for the conversion of $Be(CH_3)_2$ to liquid products decreased with increasing $B_4H_{10}/Be(CH_3)_2$ mole ratios. When $B_4H_{10}/Be(CH_3)_2$ mole ratios of ≥ 1.0 were used, further hydriding of the liquid products to solids also occurred more rapidly. For example, during an experiment in which the $B_4H_{10}/Be(CH_3)_2$ 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 B_4H_{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 $B_4H_{10}/Be(CH_3)_2$ Reactions

(C) The best conditions for the preparation of high-energy BTBH liquids appear to be the use of $B_4H_{10}/Be(CH_3)_2$ 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 re-action times are apt to yield the greatest amount of B_4H_{10} decomposition. It is possible that the action of B_4H_{10}/B_2H_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 $Be(C_2H_5)_2$ to BTBH Liquids

(C) Because of the physical state of $Be(C_2H_5)_2$, a liquid at ambient tempera-ture, it was anticipated that its reactions with B_4H_{10} might be faster and less complex than those between B_4H_{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 $(BH_3)_2[(CH_3)_m Be_{\frac{m+n}{2}} H_n]_x$ 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 BTBH SPECIES

Formula	Specific Impulse (H_2O_2), seconds	Viscosity Similarity
$(BH_3)_2(BeH_2)_4(CH_3BeH)[(CH_3)_2Be]_4$	324	Honey
$[(CH_3)_2BH]_2(BeH_2)_4[(CH_3)_2Be]_2$	315	Glycerine
$(BH_3)_2(BeH_2)[(CH_3)_2Be]_2$	316	Water

(C) Improvements in the liquid properties of the BTBH 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 B_4H_{10} with $Be(C_2H_5)_2$ served to illustrate the feasibility of this approach. This and other reactions of $Be(C_2H_5)_2$ are summarized in Table 7.

(C) $Be(C_2H_5)_2/B_4H_{10}$ Reaction. The reaction of B_4H_{10} and $Be(C_2H_5)_2$ occurred readily at ambient temperature to yield the compound $B_3H_7(C_2H_5BeH)(BeH_2)BH_3$ (specific impulse, 326 seconds). Comparison of the most likely molecular compositions of the two compounds $B_3H_7(CH_3BeH)_2BH_3$ and $B_3H_7(C_2H_5BeH)(BeH_2)BH_3$, 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 C_2H_5- substituted material was still a mobile liquid at -40 C at which temperature the CH_3- substituted material was a glass.

(C) $Be(C_2H_5)_2/B_2H_6$ Reaction. While the preparation of $B_3H_7(C_2H_5BeH)BeH_2BH_3$ demonstrated that ethyl-substituted BTBH 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)

Reactants	Mole Ratio	Comments
$B_4H_{10}/Be(C_2H_5)_2$	0.55	After a reaction time of 24 hours, a liquid was extracted from the reaction mixture. This material analyzed as $B_3H_7(C_2H_5BeH)BeH_2BH_3$.
$B_2H_6/Be(C_2H_5)_2$	0.8 and 0.4	Rapid hydriding of the metal alkyl occurred. Both $Be(BH_4)_2$ and impure BeH_2 were formed during these experiments.
$Be(BH_4)_2/Be(C_2H_5)_2$	0.8	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.
$[(C_2H_5)_2BH]_2/Be(C_2H_5)_2$	2.0	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 $(BeH_2)_x[B(C_2H_5)_3]_2$.

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 $BH_3(C_2H_5BeH)BeH_2BH_3$ from B_2H_6 and $Be(C_2H_5)_2$ was attempted (Eq. 5). Comparison of the physical state of this compound with that of $BH_3(CH_3BeH)_2BH_3$ would demonstrate more clearly the effect of ethyl groups on the physical state of BTBH liquids.

$$Be(CH_3)_2 \xrightarrow{B_2H_6} BH_3(CH_3BeH)_2BH_3 + \text{boron alkyl byproducts}$$
$$\text{(solid; melting point, 48 C)} \qquad (2)$$

$$Be(CH_3)_2 \xrightarrow{B_4H_{10}} B_3H_7(CH_3BeH)_2BH_3 + \text{boron alkyl byproducts}$$
$$\text{(liquid)} \qquad (3)$$

$$Be(C_2H_5)_2 \xrightarrow{B_4H_{10}} B_3H_7(C_2H_5BeH)BeH_2BH_3 + \text{boron alkyl byproducts}$$
$$\text{(liquid)} \qquad (4)$$

$$Be(C_2H_5)_2 \xrightarrow{B_2H_6} BH_3(C_2H_5BeH)BeH_2BH_3 + \text{boron alkyl byproducts}$$
$$\text{(physical state unknown)} \qquad (5)$$
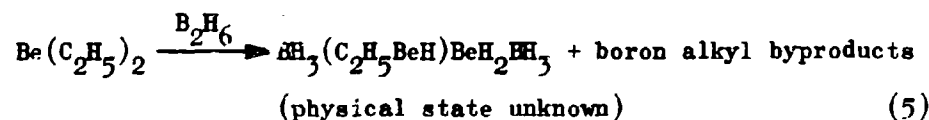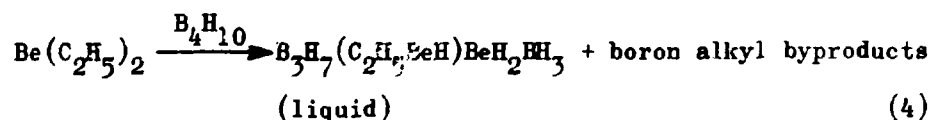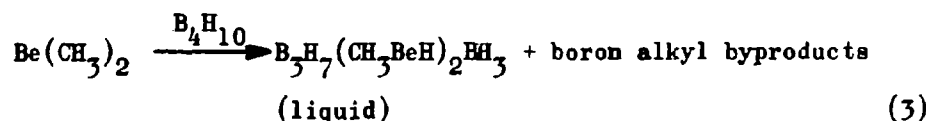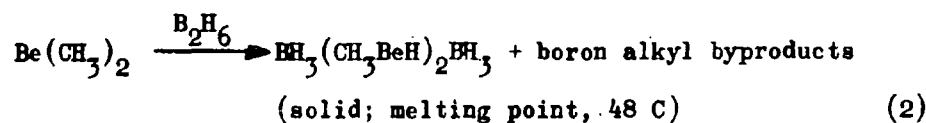
(C) The $Be(C_2H_5)_2/B_2H_6$ reaction, when conducted at mole ratios of 1.25 and 2.18, failed to yield any liquid beryllium products. Instead, the reactions proceeded rapidly to form solid boron alkyl-terminated beryllium hydride and $Be(BH_4)_2$.

(C) $Be(BH_4)_2/Be(C_2H_5)_2$ Reaction. The subsequent approach to the synthesis of a BH_3-terminated, ethyl-substituted liquid was the attempted preparation of $BH_3(C_2H_5BeH)_2BH_3$ or $(C_2H_5BeBH_4)_2$. The preparation of this compound was attempted via a method analogous to that used for the synthesis of $(CH_3BeBH_4)_2$, i.e., the reaction of the beryllium alkyl with $Be(BH_4)_2$ (1 f. 8).

(C) Rapid solution of $Be(BH_4)_2$ by $Be(C_2H_5)_2$ occurred at ambient temperature, but the reaction product was not the expected $(C_2H_5BeBH_4)_2$ (Eq. 6).

$$Be(C_2H_5)_2 + Be(BH_4)_2 \xrightarrow{\quad\times\quad} (C_2H_5BeBH_4)_2 \qquad (6)$$
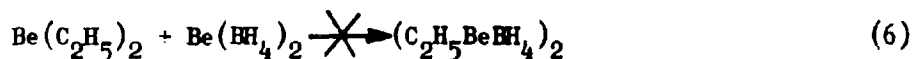
Instead of $(C_2H_5BeBH_4)_2$, a volatile liquid compound, $BH_3(C_2H_5BeH)BeH_2BH_2C_2H_5$ (specific impulse, 311 seconds), was obtained. Based on this reaction and those run between $Be(C_2H_5)_2$ and other B-H containing materials, it was evident that under comparable conditions, the $Be-C_2H_5$ bond undergoes hydriding more easily than the $Be-CH_3$ bond.

(C) Partial characterization was made of $BH_3(C_2H_5BeH)BeH_2BH_2C_2H_5$. 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 $B(C_2H_5)_3$, and nonvolatile solids.

(C) Reaction of $Be(C_2H_5)_2$ and Tetraethyldiborane. Based upon the reaction of $Be(C_2H_5)_2$ and B_2H_6 (described previously), it might be expected that alkyldiboranes would also result in the formation of "impure BeH_2". However, the reaction between $Be(C_2H_5)_2$ and tetraethyldiborane, $[BH(C_2H_5)_2]_2$, has been reported to yield a stable, liquid complex, $BeH_2[BH(C_2H_5)_2]_2$ (Ref. 9). Because there was a desire to use $BeH_2[BH(C_2H_5)_2]_2$ 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 $Be(C_2H_5)_2/[BH(C_2H_5)_2]_2$ 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 $Be-C_2H_5$ groups in the form of a complex because of incomplete hydriding of the $Be-C_2H_5$ bonds. Consequently, an experiment was conducted to establish the degree of hydriding of the $Be(C_2H_5)_2$ by the diborane derivative.

(C) A 2:1 mixture of $[(C_2H_5)_2BH]_2$ and $Be(C_2H_5)_2$ was prepared in the high-vacuum system and was permitted to warm from -196 C to ambient temperature. While

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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.

$$Be(C_2H_5)_2 + 2\ [(C_2H_5)_2BH]_2 \longrightarrow BeH_2[BH(C_2H_5)_2]_2 + 2B(C_2H_5)_3 \quad (7)$$

(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 $B(C_2H_5)_3$, was attempted by maintaining the reactor at 0 C while removi ҁ 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 $Be(C_2H_5)_2$ 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 $Be(C_2H_5)_2$ by $[BH(C_2H_5)_2]_2$ occurred in the stoichiometry shown in Eq. 6, the isolation of the reported nonvolatile $BeH_2[BH(C_2H_5)_2]_2$ 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 hydride, and volatile products other than $B(C_2H_5)_3$ 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 $BeH_2[BH(C_2H_5)_2]_2$/Beane binary systems (Ref. 10).

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 $Be(C_2H_5)_2$ 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} (BH_3 and B_3H_7). Because such BTBH liquids as $B_3H_7(C_2H_5BeH)BeH_2BH_3$ (specific im-pulse, 326 seconds), $B_3H_7(CH_3BeH)_2BeH_2BH_3$ (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) $B_4H_{10}/[(C_2H_5)_2Be \cdot C_2H_5BeH]$ Reaction. The ambient temperature decomposition of $Be(C_2H_5)_2$ (described subsequently) results in the formation of the copolymer $[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$. 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 $B(C_2H_5)_3$. The average composition of the mobile, nonvolatile liquid product was $B_3H_7(C_2H_5BeH)_4BeH_2B_3H_7$ (specific impulse, 315 seconds).

(C) $B_4H_{10}/B_2H_6/[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$ 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: $B_3H_7(C_2H_5BeH)_3BeH_2B_3H_7$ (specific impulse, 317 seconds).

TABLE 8

SUMMARY OF B_4H_{10}/ALKYLBERYLLIUM HYDRIDE REACTIONS

(Conducted at Ambient Temperature)

Reactants	Mole Ratio	Comments
$B_4H_{10}/[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$	0.6*	An ethyl-substituted BTBH liquid, $(B_3H_7)_2(C_2H_5BeH)_4BeH_2$, was isolated from the reaction mixture.
$B_4H_{10}/B_2H_6/[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$	3.7/1.0/8.4*	The addition of B_2H_6 caused an increased reaction rate and resulted in the formation of a BTBH liquid with a lower degree of polymerization. Analyses of the liquid corresponded to $(B_3H_7)_2(C_2H_5BeH)_3BeH_2$.
$B_4H_{10}/(C_2H_5BeH)_x$	0.4*	The reaction proceeded rapidly in toluene to yield insoluble solids, but no liquids.
$B_4H_{10}/B_2H_6/(CH_3BeH)_x$	2.3/1.0/5.0*	Conversion of the solid $(CH_3BeH)_x$ to a liquid occurred in 3 hours. The analyses of the reaction product indicated it to be a 48:52 mixture of $B_3H_7\{(CH_3BeH)_5[Be(CH_3)_2]_2\}B_3H_7$ and $B_3H_7\{(CH_3BeH)_6[Be(CH_3)_2]_2\}BeH(CH_3)_2$.

*The calculated values for the polymeric beryllium compounds were based on the monomer.

(C) $\underline{B_4H_{10}/C_2H_5BeH}$ Reaction. The effect of a solvent on the reaction of B_4H_{10} and alkylberyllium hydrides was investigated. For this purpose, $(C_2H_5BeH)_x$ 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 B_4H_{10} and $(C_2H_5BeH)_x$ in toluene yielded only solids, rich in Be-H species, despite the use of a small $B_4H_{10}/(C_2H_5BeH)_x$ mole ratio. The failure to obtain liquid products from this reaction is attributed to the hydriding of $(C_2H_5BeH)_x$ to $(BeH_2)_x$, and the insolubility of the $(BeH_2)_x$ in toluene. As a result, the formation and precipitation of $(BeH_2)_x$ was a more favored reaction than that involving complexing of the $(C_2H_5BeH)_x$ or $(BeH_2)_x$ by B_4H_{10}. These results are the same as those obtained from the reaction of liquid B_4H_{10} and $Be(CH_3)_2$.

(C) $\underline{B_4H_{10}/B_2H_6/(CH_3BeH)_x}$ Reaction. A B_4H_{10}/B_2H_6 mixture converted $(CH_3BeH)_x$ to a liquid in 3 hours when a $B_4H_{10}/CH_3BeH/B_2H_6$ of 2.34/5.00/1.00 was used. During this reaction time, however, little hydriding of the CH_3BeH occurred; only trace amounts of $B(CH_3)_3$ were obtained. The principal volatile product was $(CH_3BeBH_4)_2$, suggesting that the B_2H_6 caused some unzipping of the $(CH_3BeH)_x$ polymer.

(C) Analyses of the nonvolatile liquid product were best explained by assuming a 48:52 mixture of $B_3H_7(CH_3BeH)_5[Be(CH_3)_2]B_3H_7$ and $B_3H_7(CH_3BeH)_6[Be(CH_3)_2]BH(CH_3)_2$. Because end-group analyses for boron of the $(CH_3BeH)_x$, prepared from $(BeH_2)_x$ $[B(C_2H_5)_3]_2$ and $Be(CH_3)_2$, had indicated a degree of polymerization of 26, there was little doubt that its reaction with the B_4H_{10}/B_2H_6 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 $B_2H_6/B_4H_{10}/(CH_3BeH)_x$ reaction products was treated with an additional quantity of B_2H_6 and B_4H_{10} for 2.5 hours. The resulting compound analyzed as $B_3H_7(CH_3BeH)_6BH_2CH_3$.

Problems of Hydriding BTBH Liquids

(C) The reaction of B_4H_{10} or B_2H_6/B_4H_{10} mixtures with alkylberyllium hydrides failed to yield BTBH 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 $Be(CH_3)_2$ chains are Be-C-Be, 66 degrees and C-Be-C, 114 degrees. Although no structural data exist for $(BeH_2)_x$, it is presumed that the Be-H-Be angle should be greater than 66 degrees and the H-Be-H angle should be less than 114 degrees because of the better orbital overlap of the spherical s orbital of H with the two beryllium sp^3 orbitals when compared with the overlap of the narrower sp^3 orbital of carbon.

(C) On this basis, an explanation for the facile replacement of approximately one-half of the methyl groups in $Be(CH_3)_2$ (I) by hydrogen may be invoked.
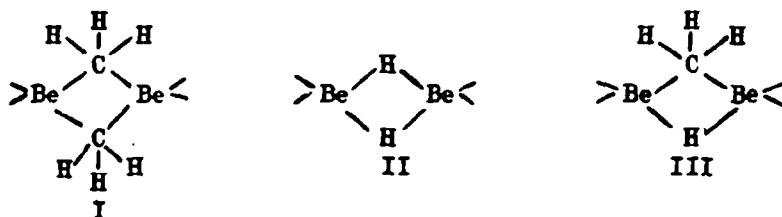
When one of the two bridging CH_3 groups of $Be(CH_3)_2$ is replaced by H, to give structure III, the tendency is for the Be atoms to move closer together, reducing the Be-C-Be angle to less than 66 degrees. The resulting increased overlap of the three sp^3 orbitals makes a stronger methyl bridge bond, and as a result, one more difficult to replace in structure III than in structure I. Consequently, even though the formation of BeH_2(II) units should be favored thermodynamically, replacement of the remaining CH_3 by H becomes kinetically controlled. Potential solutions to this problem are outlined in the Summary and Recommendations section of this report.

Reactions of Metathetical $(BeH_2)_x$

(C) Several attempts were made to prepare BTBH liquids from the reaction of metathetical $(BeH_2)_x$, synthesized from the reaction of $Al(C_2H_5)_3$ and $Be(BH_4)_2$ (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) $B_4H_{10}/(BeH_2)_x$ 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 B_4H_{10}, for example, with $(BeH_2)_x$.

(C) The reaction of B_4H_{10} and $(BeH_2)_x$ at ambient temperature during 4 days resulted in the formation of H_2 and $Be(BH_4)_2$, but no liquids. The yield of $Be(BH_4)_2$ was 20 percent (based on the beryllium hydride used), with only a 25 percent recovery of the B_4H_{10} used. The formation of $Be(BH_4)_2$ from B_4H_{10} a. $(BeH_2)_x$ at ambient temperature was undoubtedly caused by the format⋯ H_3 groups via the decomposition of B_4H_{10}.

(C) 1,2-Trimethylenediborane/BeH$_2$ Reaction. The reaction of 1,2-trimethylenediborane (Ref. 12)
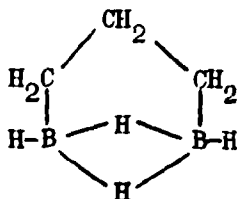
and metathetical $(BeH_2)_x$ was also investigated as a method for forming BTBH liquids. Although the reactions of $Be(BH_4)_2$ (Ref. 8), B_2H_6 (Ref. 8), and B_4H_{10} with metathetical $(BeH_2)_x$ yielded only sublimable solid products, the presence of methylene groups in the 1,2-trimethylenediborane could serve to alter the physical state of the products.

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(C) A mixture of the diborane derivative (containing some n-propyldiborane, a byproduct of the preparation of 1,2-trimethylenediborane) and metathetical $(BeH_2)_x$ 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, $Be(BH_4)_2$. No further investigation of this system was made because the main portion of the reaction mixture remained a pasty solid.

ALANE-TERMINATED BERYLLIUM LIQUIDS

(C) As a result of experiments conducted at Rocketdyne under Contract AF04(611)-9882, it was determined that Beane reacted with $Al(CH_3)_3$ 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 $Al(CH_3)_3$

(C) The reaction of Beane with $Al(CH_3)_3$ 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 $Al(CH_3)_3$

at 130 C by conducting a series of experiments in which 2:1 mixtures of $Al(CH_3)_3$ and Beane (96 percent purity) were used. The rate of disappearance of solid Beane (Fig. 1) fitted a simple second-order expression (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 $Al(CH_3)_3$ [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 $Al(CH_3)_3$/Beane reaction. After heating a 1.7:1 mixture of $Al(CH_3)_3$ 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 $[(CH_3)_2AlH]_3$, along with unreacted $Al(CH_3)_3$. The results of this experiment strongly suggest that the reaction of $Al(CH_3)_3$ and Beane occurs as a consequence of hydrogen-methyl group exchange.

(C) <u>Composition vs Reaction Time</u>. The series of experiments used for establishing the rate of reaction of Beane with $Al(CH_3)_3$ also served to indicate the variation of composition of the ATBH liquids with reaction time. While there was some scatter in the analytical data obtained with the ATBH materials, i.e., after removal of the excess $Al(CH_3)_3$ and any volatile reaction products, a trend toward decreased methyl group content in the ATBH material with reaction time was apparent. However, the best product still contained too much carbon for its use as a neat liquid fuel.
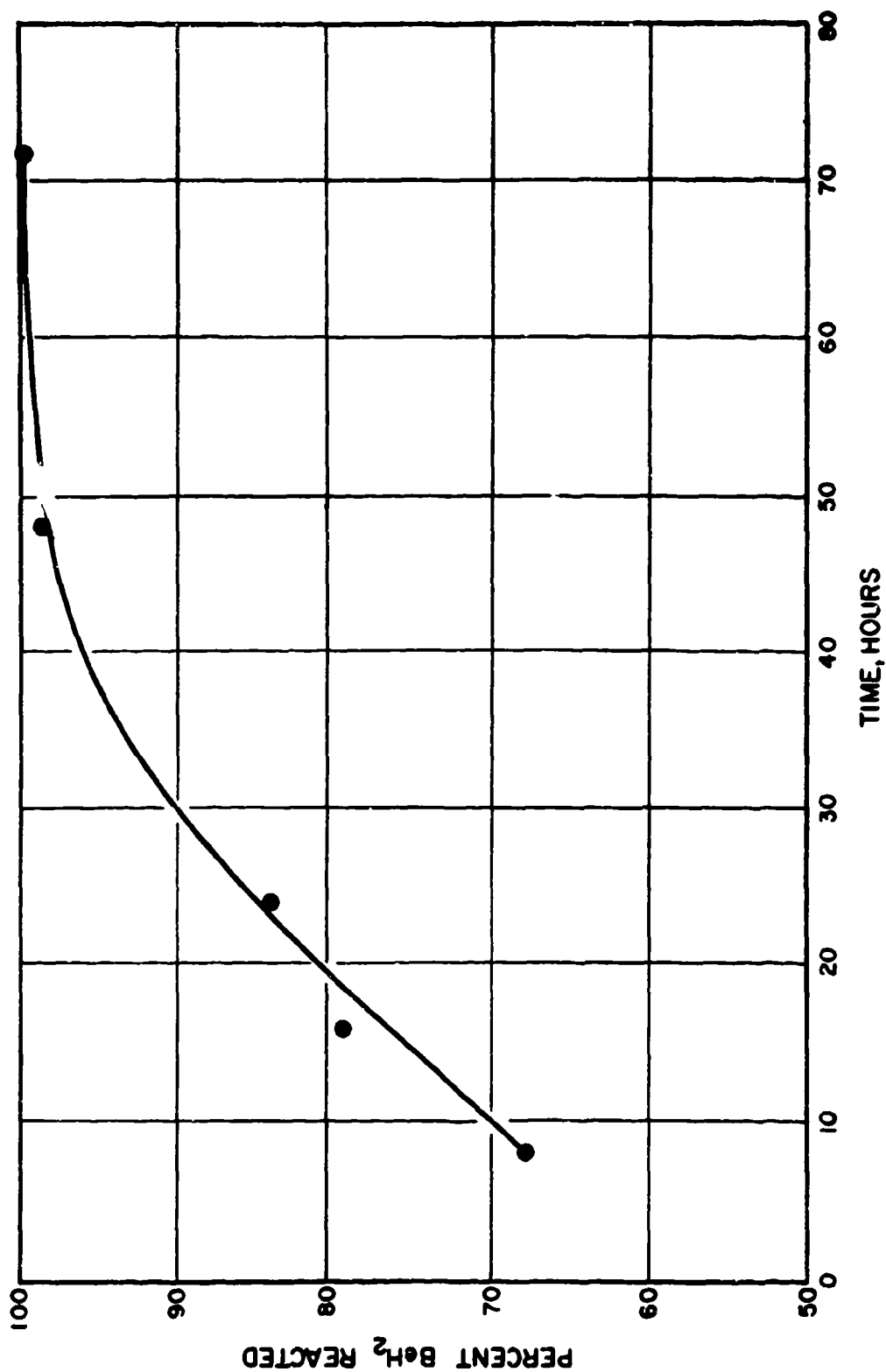
Figure 1. Rate of BeH$_2$ Reaction With Al(CH$_3$)$_3$ at 130 C

(C) <u>Nature of Insoluble Materials</u>. As stated previously, the rate of re-
action between Beane and $Al(CH_3)_3$ is temperature dependent; for example,
appreciable amounts of unreacted solids remained after short reaction
times even at 130 C (Fig. 1). The nature of the unreacted solids re-
maining after reaction of $Al(CH_3)_3$ 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 $(BeH_2)_x[Al(CH_3)_3]_2$ 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, $[(CH_3)_2AlH]_3$, 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
130 C, the amount of reaction was four times greater with $Al(CH_3)_3$ than
with the $[(CH_3)_2AlH]_3$ (21 vs 84 weight percent BeH_2 reacted.) The re-
covered 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 forma-
tion of such intermediates from $[Al(CH_3)_2]_2$ should be easier than from
$[(CH_3)_2AlH]_3$ because Al-H-Al bridge bonds are stronger than Al-CH_3-Al
bridge bonds. On this basis, the greater reactivity of $Al(CH_3)_3$ 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 BeH_2 (for example, Ref. 16), and the fact that infrared spectra of these materials are not composite spectrograms of $(CH_3)_3Al$ or $(CH_3)_2AlH$ and BeH_2 or CH_3BeH.

(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 $(CH_3)_3Al(CH_3BeH)(BeH_2)_2Al(CH_3)_3$

Density (29 C), gm/cc	0.72
Thermal Stability (as gas evolution rate), cc/min/lb	5.1×10^{-2} (71 C or 160 F) 1.2×10^{-4} (ambient temperature)
Specific Impulse (shifting equilibrium, $1000 \rightarrow 14.7$ psia, H_2O_2), seconds	297

It has been observed that the viscosity of the ATBH material can be varied simply by the addition or removal of $Al(CH_3)_3$ 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.

$$[Al(CH_3)_3]_2 + (CH_3)_3Al(CH_3BeH)_2(BeH_2)_2Al(CH_3)_3 \rightleftharpoons$$

$$2(CH_3)_3Al[(CH_3BeH)(BeH_2)]Al(CH_3)_3 \qquad (8)$$
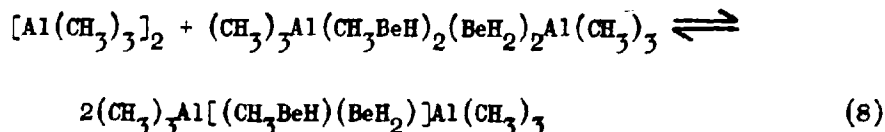
Hydriding of ATBH Liquids

(C) The quantitative reaction of $Al(CH_3)_3$ and Beane 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 B_2H_6, B_4H_{10}, and $Be(BH_4)_2$ 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
$B_4H_{10} > Be(BH_4)_2 > B_2H_6$. 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

HYDRIDING OF ATBH LIQUID

Reagent	Quantity, millimoles	Be:H:CH_3 Ratio	
		ATBH Liquids	Product
B_4H_{10}	0.429	1.0:1.0:1.85	1.0:2.9:1.0
$Be(BH_4)_2$	0.452	1.0:1.0:1.85	1.0:1.8:0.92
B_2H_6	0.455	1.0:1.0:1.85	1.0:1.5:0.93

Improved Preparations of Beryllium Alkyls

(U) The $Be(CH_3)_2$ and $Be(C_2H_5)_2$ 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 $Be(CH_3)_2$ from the magnesium
salts formed during the preparative reaction often resulted in the cosubli-
mation of an iodide-containing impurity (most likely CH_3BeI). It was
found that the iodide impurity could be converted to a nonvolatile sub-
stance by thermally soaking the crude product at 115 C. Subsequent
sublimation of the $Be(CH_3)_2$ then yielded material of 99+ percent purity.

(U) A convenient procedure for the preparation of ether-free $Be(C_2H_5)_2$ was developed during the course of this contract. It was found that if the solid reaction products of C_2H_5MgBr and $BeCl_2$ were extracted with benzene at ambient temperature, the $Be(C_2H_5)_2$ which was recovered after a simple distillation was of 99+ percent purity. The benzene extraction was found to facilitate the recovery of the $Be(C_2H_5)_2$ from the solid reaction products.

DECOMPOSITION OF $Be(C_2H_5)_2$ AT AMBIENT TEMPERATURE

(U) Although $Be(C_2H_5)_2$ 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 $Be(C_2H_5)_2$ consisted of a beryllium-containing solid and unidentified gases. Analyses of the solid revealed it to be a copolymer of $Be(C_2H_5)_2$ and C_2H_5BeH, $[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$.

(C) It has been observed at Ethyl Corporation that the binary system $Be(C_2H_5)_2/$ 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 $Be(C_2H_5)_2$ produced solids within a few days. The similarity between the behavior of neat $Be(C_2H_5)_2$, prepared by the Grignard method, which undoubtedly contained trace amounts of diethyl ether, and the Ethyl Corporation results suggests that the decomposition of $Be(C_2H_5)_2$ is catalyzed by Lewis bases.

PYROLYSIS OF $Be(C_2H_5)_2$

(C) The pyrolysis of $Be(C_2H_5)_2$ has been reported to yield a liquid compound having the composition $C(BeH_2BeC_2H_5)_4$ (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

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samples of a nonvolatile liquid product were obtained from the pyrolysis of $Be(C_2H_5)_2$ at 200 C. Although the ratios of the constituents of the pyrolysis product approached those expected for the composition $C(BeH_2BeC_2H_5)_4$, 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 $Be(C_2H_5)_2$ 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 beryllii

CONCLUSIONS AND SUMMARY

(C) This program has demonstrated that liquid beryllium hydrides may be pre-
pared with theoretical specific impulses approaching 330 seconds
$(1000 \rightarrow 14.7, H_2O_2$ oxidizer). It appears that higher borane fragments,
such as B_3H_7, are better than simple BH_3 groups as the terminating species
for these liquids, inasmuch as liquids containing B_3H_7 have good fluidity
and other satisfactory properties coupled with high impulse. Further in-
creases in BeH_2 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 B_4H_{10} with $Be(CH_3)_2$ and $Be(C_2H_5)_2$ resulted in the
synthesis of compounds such as $B_3H_7(CH_3BeH)_2BeH_2BH_3$ (329 seconds),
$B_3H_7(C_2H_5BeH)BeH_2BH_3$ (326 seconds), $B_3H_7(CH_3BeH)_3BeH_2BH_3$ (326
seconds), and $B_3H_7(CH_3BeH)_2BH_3$ (320 seconds).

2. Previously it had been observed that the termination of BTBH
liquids with two BH_3 groups often yielded materials which under-
went reversible dissociation. When one of the BH_3 groups was
replaced by a B_3H_7 terminator, the tendency of the liquids to
dissociate reversibly was eliminated.

3. The preparation of $B_3H_7(C_2H_5BeH)BeH_2BH_3$ demonstrated that it is
possible to prepare ethyl-substituted BTBH analogs of previously
known methyl-substituted liquids, and that one ethyl group re-
placing two methyl groups in such compounds leads to higher
specific impulse.

4. The preparation of liquids containing both ethyl and B_3H_7 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 ATBH 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 ATBH liquids with B_2H_6, B_4H_{10}, and $Be(BH_4)_2$ proved the feasibility of using the ATBH liquids as precursors for BTBH materials. In each of the preceding reactions, the displacement of aluminum from the ATBH 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_3H_7-terminated liquids has been the re-
actions of B_4H_{10} with various beryllium compounds. These reactions have
proved to be very complex. On the other hand, reactions of the ternary
system $B_2H_6/B_4H_{10}/Be$ 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_2H_6 concentration, and its vari-
ation, 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_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 $Be(C_2H_5)_2$ occurs much more readily than from $Be(CH_3)_2$.
This difference in the reactivity of $Be(CH_3)_2$ and $Be(C_2H_5)_2$ may serve a
useful purpose if instead of reacting B_4H_{10}, for example, with either
pure $Be(CH_3)_2$ or $Be(C_2H_5)_2$, a mixed alkyl, $CH_3BeC_2H_5$, or a copolymer of
the two alkyls is used. The reaction of either one of these materials
with a B_2H_6/B_4H_{10} mixture may result in a rapid and quantitative conversion
of the $Be-C_2H_5$ bonds to Be-H bonds, leaving the $Be-CH_3$ 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_2H_6, $Be(BH_4)_2$, and B_4H_{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.

$$2Base \cdot B_3H_7 + ATBH \text{ liquid} \longrightarrow BTBH \text{ liquid} + 2Base \cdot Al(CH_3)_3 \qquad (9)$$

$$2MB_3H_8 + ATBH \text{ liquid} \longrightarrow BTBH \text{ liquid} + 2MBA(CH_3)_3 \tag{10}$$
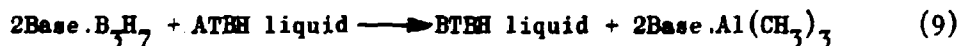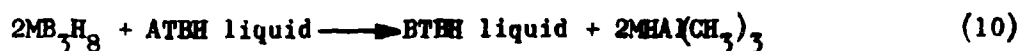
The above reactions may not only prove to be more convenient than those involving B_4H_{10} and beryllium alkyls, but may also result in the formation of pure liquid beryllium compounds, free from side products introduced from the disproportionation of B_4H_{10}.

(C) Two additional approaches to the preparation of BTBH 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_5H_9 and B_5H_{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 BTBH 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) $Be(BH_4)_2$. Beryllium borohydride was prepared by reacting $LiBH_4$-KBH_4 mixtures with $BeCl_2$ (Ref. 11).

(U) <u>Beryllium Alkyls</u>. Dimethylberyllium was prepared by the method of Gilman (Ref. 18). After thermal dissociation of the $Be(CH_3)_2$·etherate, iodide impurities were detected in the sublimed $Be(CH_3)_2$. Removal of this contaminant, possibly CH_3BeI, was accomplished by thermally soaking the crude $Be(CH_3)_2$ at 115 C. Subsequent sublimation of the material treated in this manner yielded pure $Be(CH_3)_2$.

(U) Ether-free $Be(C_2H_5)_2$ 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 $Be(C_2H_5)_2$ (boiling point, 69 C at 0.11 mm Hg) in 55 percent yield and 99+ percent purity.

(U) B_4H_{10}. Tetraborane was synthesized by the decomposition of B_2H_6 under pressure essentially as described by Kodama (Ref. 19). As determined by infrared spectroscopy, the material was pure after fractional condensation.

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(U) <u>Solvents</u>. Solvents were obtained from various commercial sources, dried over $LiAlH_4$, and stored over $LiAlH_4$ until used.

ANALYTICAL PROCEDURES

(U) 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 CH_4 or C_2H_6 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.

(U) 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.

(U) 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.

<u>Direct B-Alkyl Group Analysis</u>

(C) The analysis of BTBH liquids for boron-bound alkyl groups was developed with mixtures of $Be(CH_3)_2$ and B_2H_6. The procedure was as follows. Weighed samples of $Be(CH_3)_2$ (0.0420 gram) and B_2H_6 (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 mil-
liliters). The $B_2H_6/Be(CH_3)_2$ mixture was reacted for 18.5 hours to en-
sure equilibration of the CH_3 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 tempera-
ture were collected, after passing through a -196 C trap, and measured in
an automatic Toepler system. All materials not passing -196 C were re-
turned 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-CH_3 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. Cal-
culated were: Be, 1.07 matoms; B, 1.89 matoms; hydridic hydrogen, 5.66
mmoles; and total CH_3 groups, 2.14 mmoles. Found were: Be, 1.02 matoms;
B, 1.89 matoms; hydridic hydrogen, 5.60 mmoles; and total CH_3 groups, 2.18
mmoles.

$B_4H_{10}/Be(CH_3)_2$ REACTIONS

Physical State of B_4H_{10} and its Reactivity

(C) The experiments conducted to determine how the physical state of B_4H_{10}
altered its reaction with $Be(CH_3)_2$ were performed in the following manner.
To a heavy-wall cylindrical reactor containing $Be(CH_3)_2$ (0.3535 gram,
9.05 mmoles) was added liquid B_4H_{10} (0.4794 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_4H_{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_4H_{10} and alkylboron products. The results of the reactions are presented in Table 11.

TABLE 11

REACTION OF $Be(CH_3)_2$ WITH B_4H_{10} VAPOR AND WITH LIQUID B_4H_{10}
(Reaction Time 29.5 hours at Ambient Temperature)

Reactants, mmoles	Volatile Products,* mmoles					Nonvolatile Products, grams
	H_2	$(CH_3)_2B_2H_4$	$(CH_3)_4B_2H_2$	$B(CH_3)_3$	B_4H_{10}	
$Be(CH_3)_2$, 9.15	2.50	1.13	0.17	1.94	3.35	Liquid, 0.3913
B_4H_{10} (vapor), 8.94						Solid, 0.0586
$Be(CH_3)_2$, 9.05	2.08	--	--	3.46	4.42	Solid, 0.0154
B_4H_{10} (liquid), 8.99						Liquid, 0.040

*In addition to the tabulated volatile products, trace amounts of $(CH_3BeBH_4)_2$, $Be(BH_4)_2$, 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_4 (0.35 mmole). The observed $Be:B:H:CH_3$ ratios were 3.84:6.00:16.0:2.10; calculated for $[(CH_3)_3B_3H_4]_2(BeH_2)_2(CH_3BeH)_2$ 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_3 ratios were 3.84:6.00:16.0:2.10; calculated for $[(CH_3)_3B_3H_4]$(BeH$_2$)$_2$(CH$_3$BeH)$_2$ 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_3 ratios derived from these results were: 3.02:4.00:13.8: , calculated for B_3H_7(CH$_3$BeH)$_2$BeH$_2$BH$_3$ 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_3 ratios of 2.00:4.04:11.6:1.72 approached those calculated for B_3H_7(CH$_3$BeH)$_2$BH$_2$CH$_3$, i.e., 2:4:12:2.

B_4H_{10}/B_2H_6/$(CH_3)_2$Be 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

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TABLE 12

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

Experiment No.	Reactants, moles	Reaction Time, hours	Volatile Products, moles									Nonvolatile Products, grams
			B_2H_6	H_2	B_4H_{10}	B_5H_{11}	$B(CH_3)_3$	$CH_3B_2H_5$	$(CH_3)_2B_2H_4$	$(CH_3)_4B_2H_2$	$Be(BH_4)_2$	
1	$Be(CH_3)_2$, 9.99 B_4H_{10}, 13.0	93	—	4.42	trace	0.35	—	0.30	3.66	0.95	4.55	Solids, 0.5102
2	$Be(CH_3)_2$, 9.15 B_4H_{10}, 8.94	29	—	2.50	3.35	—	1.94	—	1.15	0.17	trace	Solids, 0.0986 Liquid, 0.3913
3	$Be(CH_3)_2$, 9.90 B_4H_{10}, 19.82	29	0.24	5.57	9.04	0.04	0.11	0.05	3.70	—	—	Solids, 0.3798
4	$Be(CH_3)_2$, 18.1 B_4H_{10}, 9.2	120	—	2.35	0.95	—	5.17	—	—	—	—	4, 0.392 unweighed
5	$Be(CH_3)_2$, 18.0 B_4H_{10}, 9.3	120	—	2.38	Volatile products neither measured nor identified							Solids, unweighed (?)

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TABLE 13

SUMMARY OF $B_4H_{10}/B_2H_6/Be(CH_3)_2$ REACTIONS

Experiment No.	Reactants, mmoles	Reaction Time, hours	Volatile Products, mmoles					Nonvolatile Products, grams
			H_2	B_2H_6	B_4H_{10}	$B(CH_3)_3$	$(CH_3BeH_4)_2$	
1	$Be(CH_3)_2$, 3.87 B_4H_{10}, 3.72 B_2H_6, 0.92	8	0.12	0.14	3.06	0.70	0.40	Liquid, 0.1191
2	$Be(CH_3)_2$, 4.03 B_4H_{10}, 4.27 B_2H_6, 1.25	7.5	Neither measured nor identified					Liquid, 0.1222
3	$Be(CH_3)_2$, 4.81 B_4H_{10}, 4.89 B_2H_6, 1.25	15.3	0.39	—	3.89	1.17	0.88	Liquid, 0.20

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estimated by material balance. The formulas derived for these materials were B_3H $(CH_3BeH)_2$ $[(CH_3)_2Be]_3BH_3$ (experiment No. 1) and $B_3H_7[Be(CH_3)_2]_2$ $(CH_3BeH)_2BH_3$ (experiment No. 3).

(C) <u>Analysis of Liquid Product, Experiment 2</u>. 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 $B_3H_7(CH_3BeH)_2$ $Be(CH_3)_2BH_3$ and $B_3H_7(CH_3BeH)_4BH_2CH_3$ (0.0266-gram sample) were as follows. Found were: Be, 0.57 matom; B, 0.63 matom; H_2, 2.25 moles; CH_4, 0.62 mmole; and B-alkyl CH_4, 0.10 mmole. Calculated were: Be, 0.61 matom; B, 0.68 matom; H_2, 2.30 mmoles; CH_4, 0.68 mmole; and B-alkyl CH_4, 0.10 mmole.

$Be(C_2H_5)_2$ B_4H_{10} Reaction

(C) $Be(C_2H_5)_2$ (0.841 gram, 12.5 mmoles) was treated with B_4H_{10} (6.9 mmoles) 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 (2.03 mmoles) was removed. The volatile products were then removed and identified as being primarily $[(C_2H_5)_2BH]_2$ (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 $B_3H_7(C_2H_5BeH)BeH_2BH_3$.

(C) Analyses f $B_3H_7(C_2H_5BeH)BeH_2BH_3$ (0.0350-gram sample) were as follows. Calculated (in mmoles) were: Be, 0.68; B, 1.35; hydridic hydrogen, 4.73; and hydroly C_2H_5 groups, 0.34. Found were: Be, 0.63; B, 1.38; hydridic hy gen, 4.42; and hydrolyzable C_2H_5 groups, 0.30.

$Be(C_2H_5)_2/B_2H_6$ Reaction

(C) The first reaction was carried out by condensing B_2H_6 (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 $(C_2H_5)_2B_2H_4$ (1.68 mmoles), $B(C_2H_5)_3$ (0.72 mmole, and $Be(BH_4)_2$ (1.87 mmoles). A sample (0.0270 gram) of the nonvolatile solid recovered (0.1946) when hydrolyzed yielded H_2 (1.23 mmoles), C_2H_6 (0.01 mmole), Be(0.50 matom, and B(0.18 matom), indicating that the solid was essentially $(BeH_2)_6 \cdot [B(C_2H_5)_3]_2$.

(C) The second reaction utilized a larger $Be(C_2H_5)_2/B_2H_6$ mole ratio (3.78/1.42). The reaction was halted after 18 hours. The reaction products were $B(C_2H_5)_3$ (1.74 mmoles), $Be(BH_4)_2$ (0.33 mmole), and a nonvolatile solid (0.0894 gram). A sample (0.0224 gram) of the nonvolatile solid when hydrolyzed yielded H_2 (1.69 mmoles), C_2H_6 (0.06 mmole), Be(0.71 matom), and B (0.16 matom) indicating again the formation of a boron alkyl-terminated beryllium hydride.

$Be(BH_4)_2/Be(C_2H_5)_2$ Reaction

(C) Beryllium borohydride (1.382 grams, 35.8 mmoles) was added to a reactor containing $Be(C_2H_5)_2$ (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 $B(C_2H_5)_3$ (amount not measured) and an unknown were distilled. Isolation of the unknown from $B(C_2H_5)_3$ 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 $C_2H_5BH_2BeH_2(C_2H_5BeH)BH_3$. Found (0.0793 gram sample) in mmoles were. Be, 1.30; B, 1.45; hydridic hydrogen, 6.0; and hydrolyzable C_2H_5 groups, 0.82. Calculated in mmoles were: Be, 1.50; B, 1.50; hydridic hydrogen, 6.0; and hydrolyzable C_2H_5 groups 0.75.

Reaction of $Be(C_2H_5)_2$ and Tetraethyldiborane

(C) <u>Simple Mixing</u>. A 2:1 mixture of the reactants was prepared by condensing at -196 C, tetraethyldiborane (0.2985 gram, admixed with 5 weight percent of triethyldiborane 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 H_2 and 0.1 mole percent C_2H_6. The quantity of hydrogen collected was in agreement with that expected (4.45 mmoles) based on analysis of the tetraethyldiborane. The absence of ethane in any appreciable quantities illustrated the near-quantitative hydriding of the beryllium.

(C) Attempted Isolation of $BeH_2[BH(C_2H_5)_2]_2$. An aliquot of the tetraethyldiborane (0.4803 gram) used previously and $Be(C_2H_5)_2$ (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 C_2H_5 groups, 0.38 mmole. The nonvolatile fraction contained: Be, 0.79 matom; B, 0.23 matom; hydridic hydrogen, 2.44 mmoles; and hydrolyzable C_2H_5 groups, 0.09 mmole.

(C) A third experiment in which $Be(C_2H_5)_2$ (1.65 mmoles) was added in the liquid state to $[BH(C_2H_5)_2]_2$ (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 C_2H_5 groups, 0.06 mmole;

nonvolatile fraction: Be, 0.65 matom; B, 0.48 matom; hydridic hydrogen, 2.22 mmoles; hydrolyzable C_2H_5 groups, 0.01 mmole.

$B_4H_{10}/[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$ Reaction

(C) The copolymer $[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$ (0.7369 gram, 7.50 matoms of Be) was treated with B_4H_{10} (4.82 mmoles) for 94 hours. The volatile products were H_2 (1.43 mmoles) and $B(C_2H_5)_3$ (2.31 mmoles); B_4H_{10} (0.53 mmole) was also recovered. The nonvolatile liquid product was treated with an additional quantity of B_4H_{10} (1.54 mmoles) for 23 hours, after which time H_2(0.23 mmole), B_4H_{10} (0.70 mmole) and $B(C_2H_5)_3$ (0.32 mmole) 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 H_2 (2.85 mmoles), B (0.0085 gram, 0.79 matom), Be (0.0061 gram, 0.68 matom), and hydrolyzable C_2H_5 groups, as ethane, (0.54 mmole). This results in Be:B:H:C_2H_5 ratios of 5.0:5.8:21.0:4.0; calculated for $(B_3H_7)_2(C_2H_5BeH)_4BeH_2$ are: 5:6:22:4.

$B_4H_{10}/B_2H_6/[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$ Reaction

(C) Treatment of a $[(C_2H_5)_2Be \cdot C_2H_5BeH]_x$ sample (0.6707 gram, 12.2 matoms of Be) with a mixture of B_4H_{10} (5.31 mmoles) and B_2H_6 (1.45 mmoles) resulted in liquefaction of the copolymer in less than 48 hours. The volatile products were H_2 (1.42 mmoles) and $B(C_2H_5)_3$ (3.08 mmoles); B_4H_{10} (1.07 mmoles) 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) Analyses of a sample (0.0214 gram) of the liquid yielded H_2 (1.95 mmoles), B (0.0064 gram, 0.59 matom), Be (0.0034 gram, 0.38 matom), and hydrolyzable

C_2H_5 groups, as ethane, (0.29 mmole). This results in $Be:B:H:C_2H_5$ 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} 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_6 (2.55 mmoles), and Be (22.9 mg, 2.54 matoms). 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.

$B_4H_{10}/B_2H_6/(CH_3BeH)_x$ 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 $[CH_3BeH]_{21}[Be(CH_3)_2]_5[B(C_2H_5)_3]_2$.

(C) A sample of the preceding compound (0.3858 gram, 11.0 matoms 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 $(CH_3BeBH_4)_2$ (2.01 mmoles).

(C) The residual liquid was analyzed 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 $B_3H_7(CH_3BeH)_5[Be(CH_3)_2]$- B_3H_7 and $B_3H_7(CH_3BeH)_6[Be(CH_3)_2]BH(CH_3)_2$ were as follows. Found were: Be, 0.68 matom; B, 0.42 matom; H_2, 1.87 mmoles; CH_4, 0.79 mmole; and B-alkyl CH_4, 0.11 mmole. Calculated were: Be, 0.68 matom; B, 0.42 matom; H_2, 1.86 mmoles; CH_4, 0.78 mmole; and B-alkyl CH_4, 0.11 mmole.

(C) A sample of the above liquid mixture (0.0528 gram) was treated with additional B_4H_{10} (1.16 mmoles) and B_2H_6 (0.12 mmole) 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 $B_3H_7(CH_3BeH)_6BH_2CH_3$. Found were: Be, 0.70 matom; B, 0.46 matom; H_2, 1.86 mmoles; and CH_4, 0.71 mmole. Calculated were: Be, 0.69 matom; B, 0.46 matom; H_2, 1.85 mmoles; and CH_4, 0.71 mmole.

$B_4H_{10}/(BeH_2)_x$ Reaction

(C) Tetraborane (4.95 mmoles) was added to a reactor containing boron alkyl-terminated BeH_2 (0.0785 gram, 65.1 percent purity, 4.6 mmoles of BeH_2). After a reaction time of 4 days, hydrogen (2.45 mmoles), unreacted B_4H_{10} (1.80 mmoles), B_2H_6 (0.09 mmole), $Be(BH_4)_2$ (0.0347 gram, 0.9 mmole), and trace amounts of ethyldiboranes were recovered.

1,2-Trimethylenediborane/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_3H_6 (64 millimeters), B_2H_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 B_2H_6 by fractional condensation at
-97 C. Infrared and hydrolytic analyses of the product indicated a mix-
ture of 1,2-trimethylenediborane (70 percent) an n-propyldiborane (30
percent). This mixture was used without further purification.

(C) An analyzed sample of $(BeH_2)_x(BH_3)_2$ (0.0612 gram, 4.0 mmoles of BeH_2) was
treated at ambient temperature with the impure 1,2-trimethylenediborane
(0.3076 gram, 3.15 mmoles). 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 $Al(CH_3)_3$

(C) The reactivity of Beane with $Al(CH_3)_3$ 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 $Al(CH_3)_3$ 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 $Al(CH_3)_3$
(Table 14).

(C) The insoluble solid, remaining from the $Al(CH_3)_3$/Beane reaction, was
identified in the following manner. A mixture of Beane (0.50 gram) and
$Al(CH_3)_3$ (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 (3.80 mmoles) and aluminum (< 0.1 mg). The recovered Beane,
based on the beryllium result, was 92 percent pure.

TABLE 14

REACTION OF BEANE AND $Al(CH_3)_3$ AT 130 C

Heating Time, hours	Beane Used, milligrams*	$Al(CH_3)_3$ Used, milligrams	Beane Recovered, milligrams	Beane Reacted, percent
8	50.9	638.8	17.8	67.7
16	54.6	677.5	13.0	79.4
24	50.9	637.8	9.8	84.0
48	55.7	680.4	3.0	98.6
72	55.2	685.2	2.4	99.7

*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

Heating Time, hours	Weight of Product, milligrams	Analyses, mole ratios			
		Al	Be	H	CH_3
8	113.7	2	6.5	9.3	10.5
16	131.8	2	5.5	8.4	8.6
24	160.1	2	5.7	9.1	8.8
48	152.7	2	6.6	11.6	9.4
72	168.5	2	6.6	10.4	8.5

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), $(CH_3)_2AlH$ (33.5 percent), and CH_3BeH (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) B_2H_6 Reaction. A 2-milliliter aliquot of the standard ATBH material was pumped to constant weight (0.1185 gram) and subsequently treated with B_2H_6 (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 $B(CH_3)_3$ (0.06 mmole) and an aluminum-containing liquid. Analysis of the nonvolatile viscous material revealed the Be:H:CH$_3$ 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) $Be(BH_4)_2$ Reaction. A sample (0.1204 gram) of the ATBH material, as obtained above for the previous reaction, was treated with $Be(BH_4)_2$ (0.0175 gram, 0.452 mmole) at ambient temperature. The viscous ATBH 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:CH$_3$ ratio of 1:1.8:0.92, while the volatile fraction contained 82 percent of the aluminum.

(c) B_4H_{10} Reaction. A third sample (0.1213 gram) of the prepared ATBH liquid was treated with B_4H_{10} (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 non-volatile fractions which were subsequently analyzed. The volatile portion contained approximately 85 percent of the aluminum while the nonvolatile liquid material had Be:H:CH$_3$ ratios of 1.0:2.9:1.0.

Decomposition of $Be(C_2H_5)_2$ at Ambient Temperature

(U) The precipitate formed during ambient temperature storage of $Be(C_2H_5)_2$ 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 $(C_2H_5)_2Be \cdot C_2H_5BeH$ 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 $Be(C_2H_5)_2$

Sample Size, mg	H_2, mmoles	CH_4, mmoles	C_2H_6, mmoles	Be, matoms	Be:H:C_2H_6:CH_4 Ratios	Material Balance, percent
139.2	2.39	0.39	1.28	2.92	8.0:6.5:3.5:1.1	51.6
91.8	1.50	0.22	0.82	1.68	8.0:7.1:3.9:1.1	47.7

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(U) Samples of the crude product were twice-distilled at 90 to 95 C
(5 x 10^{-4} 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 $Be(C_2H_5)_2$

Expt. No.	Sample Size, mg.	H_2, mmoles	CH_4, mmoles	C_2H_6, mmoles	Be, matoms	$Be:H:C_2H_6:CH_4$ Ratios	Material Balance Percent
1	66.3	1.58	0.22	0.84	1.54	8.0:8.2:4.4:1.1	65.1
2	51.7	1.09	0.26	0.98	1.31	8.0:6.7:6.0:1.4	87.6
3	60.6	1.52	0.23	0.77	1.55	8.0:7.9:4.0:1.2	68.2

(U) 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 mix-
ture. 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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13. 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 $B_3H_7(CH_3BeH)_2BeH_2BH_3$ (specific impulse, 329 seconds with H_2O_2). The use of B_2H_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_3H_7-(C_2H_5BeH) BeH_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_2H_6, B_4H_{10}, or $Be(BH_4)_2$ demonstrated the feasibility of employing ATBH materials as precursors for BTBH liquids (C)

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
High-Energy Fuels						
Hydrides						
Liquid Metal						
Beryllium						
Borane						
Alane						

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