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CALLERY CHEMICAL COMPANY UNCLASSIFIED

SR-DS-3577X

Serial No. AB-9

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October 11, 1963

MONTHLY PROGRESS REPORT NO. 7

RS 3427

to

Sandia Corporation

from

Callery Chemical Company

THIS DOCUMENT CONSISTS OF 7 PAGE(S)
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SANDIA SYSTEMATIC DECLASSIFICATION REVIEW

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Submitted by:

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CLASSIFICATION CHANGED TO: U	AUTHORITY: W.C.Layne
Carmela Gallegos 11/12/97	RECORD ID: 98SN0427
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CALLERY CHEMICAL COMPANY

RESEARCH & DEVELOPMENT DIVISION · CALLERY, PA. · EVANS CITY 3510 · TWX-EVANS CITY 136

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Serial AB-8
October 11, 1963
Page 1

Sandia Corporation
Post Office Box 5800
Albuquerque, New Mexico

Attn: Mr. E. B. Bergquist, 4321

Ref. Sym: 4333/142, P. O. 13-5966

Dear Mr. Bergquist:

The following constitutes the seventh monthly report for the period September 1 to September 30, 1963, as required under purchase order 13-5966:

Experimental investigation was continued on Phase I, Part C of the program. Presently our efforts have been devoted to the preparation of aminoborane decamer, $(BH_2NH_2)_{10}$, and the determination of the thermal stabilities of the systems lithium borohydride-sulfur and lithium borohydride-ammonium chloride.

Four attempts to prepare aminoborane decamer, $(BH_2NH_2)_{10}$, had only limited success. Although the aminoborane decamer has been identified by x-ray analysis, yields have been poor and the product has been contaminated with aminoborane trimer, the unexpected major reaction product. A re-evaluation of the preparative method has resulted in an approach that should produce aminoborane decamer in good yields.

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The rate of decomposition at 165°F of the systems lithium borohydride-sulfur and lithium borohydride-ammonium chloride are too high for these systems to be of any value for this program.

BACKGROUND

The preparation of aminoborane decamer, $(BH_2NH_2)_{10}$, was reported[1] by Shore at a recent BN symposium. Experimental details of this work were not reported because the system is still under study at Ohio State. In general, the preparation consists of reacting diborane (B_2H_6) with sodium amide ($NaNH_2$) in liquid ammonia. The reaction probably proceeds through several steps, the first being the formation of the diammoniate of diborane according to the equation:

$$B_2H_6 + 2\,NH_3 \longrightarrow \left[BH_2(NH_3)_2\right]\left[BH_4\right]$$

The sodium amide then abstracts a proton from a coordinated ammonia of the diammoniate of diborane to form sodium borohydride and apparently $NH_3BH_2NH_2$ which then splits out ammonia in the self-association process as represented as follows:

$$n(NH_3BH_2NH_2) \longrightarrow NH_3(BH_2NH_2)_n + (n-1)NH_3$$

The final step is thought to be the elimination of ammonia by cyclization, resulting in the precipitation of the aminoborane decamer. Cyclization could also be induced by pumping away ammonia from a clear solution. The product is purified by sublimation at 150°C and in some cases by recrystallization from dimethylsulfoxide, the only known solvent for the material.

Shore reports the product distribution for the reaction to be generally as follows:

$(BH_2NH_2)_{10}$	-	83% minimum
$(BH_2NH_2)_3$	-	15% maximum
Unknown	-	2% maximum

1. Shore, Sheldon G., et al, The Preparation and Self-Association of BH_2NH_2 Units, Department of Chemistry, The Ohio State University, Columbus 10, Ohio. Presented at The International BN Symposium, Durham, N. C., April 1963.

Unfortunately, several areas of this preparation are not well defined. For example, the time, temperature and concentration requirements to induce self-association beyond trimerization are not reported. (If elimination of ammonia occurs with a chain of only three aminoborane units, a stable entity is formed that cannot be converted to aminoborane decamer.) Other unknowns in this preparation are the treatments of the reaction products before sublimation and the actual conditions of sublimation.

EXPERIMENTAL

Aminoborane Decamer Preparation

Four runs were made in an attempt to produce enough aminoborane decamer for thermal stability studies. Various reaction times and temperatures, hold times and temperatures and rates of ammonia removal were used in attempts to obtain a reasonable yield of aminoborane decamer. In a typical run (2705-6), 10.3 grams of sodium amide (95.5% based on ammonia evolution) was charged in a dry box to a one liter, three neck flask. The flask was then attached to a special vacuum system and 900 ml of liquid ammonia was condensed in at -78°C. Diborane (8.3 grams) diluted with nitrogen was fed under the liquid level over a period of thirteen hours with the reactor temperature held at -78°C. After standing at a temperature of -78°C for eighteen hours, the reaction mixture was allowed to warm slowly with the ammonia evaporating over a period of 72 hours. The reaction products were dried for several hours *in vacuo* to remove any adsorbed ammonia. The solid residue was then sublimed *in vacuo* for thirteen hours at 160°C. Sublimate samples collected at room temperature, -78°C and 196°C were weighed and then analyzed by x-ray, infrared and micro analytical techniques.

Thermal Stability--Lithium Borohydride-Sulfur System

A mixture consisting of 5.69 grams of lithium borohydride and 4.31 grams of sulfur was prepared in a dry box. 5.94 grams of this mixture was charged to a metal thermal stability bomb with a free volume of 90.5 ml. The bomb was attached to a vacuum system and evacuated. The bomb was placed in a 165°F constant temperature bath where the pressure in the bomb rose beyond the 15 PSIG gage limit in 24 hours. The bomb was then removed from the bath and the condensible and non-condensibles measured and analyzed.

Thermal Stability--Lithium Borohydride-Ammonium Chloride

A mixture of 2.91 grams of lithium borohydride and 7.13 grams of ammonium chloride was charged to an 86.8 ml thermal stability bomb. After 63 hours at 165°F, the pressure in the bomb exceeded the 15 PSIG gage limit. Both condensibles and non-condensibles were measured and analyzed.

RESULTS

Aminoborane Decamer Preparation

The sublimed products recovered from all four runs this month gave evidence of containing only small amounts of aminoborane decamer. X-ray analysis of the sublimates recovered at room temperature indicated that the main product was aminoborane trimer with a small amount of aminoborane decamer, the reverse of that expected from the work of Shore. The sublimates collected at -78°C and -196°C were amorphous or polymeric by both X-ray and infrared analyses. Elemental analyzes of the various fractions are very inconsistent as shown by the following results for Run 2705-6.

Temperature of Sublimate Collection	B mat/g	H mat/g	N mat/g	C mat/g	% Accountability
Room temperature	31.8	138	29.5	2.9	93
-78°C	34.3	120	31.4	1.6	95
-196°C	35.6	143	31.2	<1	97
Theory for BH_2NH_2	34.7	139	34.7	0	

The inconsistency in analytical accountabilities indicates problems in analytical techniques. The problem is probably caused by the lack of solubility of the aminoborane decamer which would affect the nitrogen analysis because it is a digestive technique. The boron and hydrogen value are determined by combustion and should not be affected by solubility.

Thermal Stability--Lithium Borohydride-Sulfur

The mixture of lithium borohydride-sulfur evolved 6.63 mmole of non-condensible gas (99.7% H_2 by mass spectrophotometer) in 24 hours at 165°F. Based on the 0.30 gram moles of hydrogen contained in the sample, this amounts to 495 standard cc of H_2 evolved/gram mole of contained H_2 in 24 hours.

Thermal Stability--Lithium Borohydride-Ammonium Chloride

The sample of lithium borohydride-ammonium chloride evolved 49.3 mmoles of non-condensible gas (99.5% H_2 by mass spectrophotometer) in 63 hours at 165°F. Based on the 0.51 gram moles of hydrogen contained in the sample, this amounts to 2165 standard cc of H_2 evolved/gram mole of contained hydrogen in 63 hours.

DISCUSSION

The attempts to prepare enough aminoborane decamer for thermal stability studies have been unsuccessful. In order to expedite this preparation, Dr. Shore was contacted at Ohio State in order to clarify some of the preparative problems. This contact has led to a better understanding of the requirements for the preparation and has resulted in an approach that should produce good yield of the aminoborane decamer.

After the diborane is added, an aging period of about 12 hours is required for the self association process to occur. After this time cyclization by elimination of ammonia is induced by removal of the ammonia solvent from the clear solution. The solid residue is then redissolved in liquid ammonia and at this point only the by-product sodium borohydride and aminoborane trimer should go into solution. The aminoborane decamer is then filtered out of the solution, washed with a solvent such as diethyl ether to remove ammonia, dried and then sublimed. This sublimation should result in a very pure product. Although in our runs we probably produced reasonable quantities of aminoborane decamer, it was probably destroyed during sublimation by reacting with sodium borohydride and/or ammonia. The redissolving of the product in ammonia and then filtering should remove all materials that are soluble in ammonia because of ammonia coordination.

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FUTURE WORK

1. Continue the investigation for other BNH hydrogen generating systems.

2. Prepare aminoborane decamer and determine its thermal stability at 165°F.

Very truly yours,

CALLERY CHEMICAL COMPANY

RB Cruikshank

R. B. Cruikshank
Project Leader

RBC/gg

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