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TECHNICAL RESEARCH REPORT

STUDIES ON THE

PREPARATION OF CALCIUM BOROHYDRIDE,

AND ON ALUMINUM CHLORIDE ETHERATE

A FINAL REPORT

BY

H. W. STONE	BRUCE GRIGGS
R. L. PECSOK	R. MEEKER
E. F. C. CAIN	D. NAIL
R. GREEN	M. RING
I. PEARSON	

UNIVERSITY OF CALIFORNIA, LOS ANGELES

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Project Directors · Hosmer W. Stone and Robert L. Pecsok

Project Personnel : E. F. C. Cain, Robert Green, Bruce Griggs,
Robert Meeker, Donald Nail, Irving Pearson,
and Morey Ring

Approved by Hosmer W. Stone

Approved by Robert L. Pecsok

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Investigation of the Reaction between Calcium Hydride and Methyl Borate as a Possible Source of Calcium Borohydride

Objective: Since sodium hydride and methyl borate react to give sodium borohydride, the analogous reaction with calcium hydride was investigated as a possible method of obtaining calcium borohydride from readily available and relatively inexpensive starting materials.

Summary and Conclusions: Three different experimental approaches were investigated:

1. Methyl borate was refluxed over calcium hydride at 250°-275°C.
2. Methyl borate and calcium hydride were placed in a hydrogenation bomb and heated to 250° to 350°C, with and without hydrogen pressure.
3. Methyl borate vapor in a carrier stream of hydrogen was passed through calcium hydride in a combustion tube at 425°C. and 485°C.

The first method gave no reaction. The second gave indication of the desired reaction with significant yields of calcium borohydride, although none was isolated. The third method resulted in a number of volatile products, but the presence of boranes could not be confirmed with the mass spectrograph.

The second method offers some promise and merits further investigation.

Experimental: The first procedure which was tried was similar to that proposed by Schlesinger, Brown, and Finholt, J. Am. Chem. Soc., 75, 205 (1953), for the preparation of sodium borohydride. A similar apparatus was set up and the reaction attempted at 250° to 275°C. Powdered calcium hydride was heated to 275°C and the methyl borate was added dropwise through a condenser. The methyl borate did not react and flooded the condenser. Several attempts were made at slightly different temperatures and with several high capacity condensers. There was no evidence that any reaction had taken place.

An alternative procedure was devised utilizing a high pressure hydrogenation bomb. In this manner the methyl borate could be kept in contact with the calcium hydride at elevated temperature. The bomb was filled under nitrogen in a dry box and a few steel balls added to facilitate mixing. The sealed bomb was heated slowly and a temperature-pressure curve was plotted. A definite break in this curve occurred at a point corresponding to 255°C and 950 p.s.i., indicating the evolution of a gaseous product. A second temperature-pressure curve was obtained from another sample; however, the break occurred at 330°C. Since the conditions were presumably identical, no explanation can be advanced for this change in the temperature of the break in the pressure curve. Qualitative examination of the gas established that it was probably hydrogen; there was no indication of the presence of borohydride in the solid remaining. Determinations of active hydrogen by evolution in both 6 N HCl and 0.1 N NaOH gave essentially the same results. Assuming that calcium borohydride is stable in 0.1 N NaOH, all active hydrogen is thus accounted for by the excess hydride. Attempts to separate the product by extraction with dioxane, diethyl ether, and isopropyl amine were unsuccessful.

The next approach was to carry out the reaction as described above, except under hydrogen pressure. Several runs were made with different hydrogen pressures up to 3500 p.s.i. In each case, a white fluffy solid product was obtained. Solvents known to dissolve other borohydrides such as diethyl ether, isopropyl amine, and tetrahydrofuran, were used in attempts to extract any calcium borohydride that may have been formed. Nothing was extracted by the above solvents, although the product reacted slowly with water to evolve hydrogen. Addition of hydrochloric acid to the water solution caused further evolution of hydrogen. The product was insoluble in 95% ethanol, and decolorized iodine in absolute methanol, a

reaction characteristic of borohydrides. The desired reaction had apparently proceeded to some extent, even though a pure compound was not separated.

The reaction was also carried out with an excess of methyl borate at 275°C. under hydrogen pressure for 48 hours. The excess methyl borate was then evaporated at 1 mm. Hg. pressure, leaving a white, extremely light and fluffy product having a molar ratio of B/Ca of 2.13. This product was apparently a mixture of the di-addition product, $\text{CaH}_2 \cdot 2 \text{B}(\text{OCH}_3)_3$, and calcium borate. Attempts to purify it by extraction with diethyl ether, dioxane, tetrahydrofuran, and isopropyl amine were unsuccessful.

A number of runs were made at 280°C. with and without hydrogen pressure, both with excess hydride and excess methyl borate. Using liquid ammonia as a solvent, small amounts of product were isolated from crude products made with excess hydride. This product was contaminated with residual ammonia. It was slightly soluble in water without decomposition; however, it was decomposed rapidly by hydrochloric acid with hydrogen evolution. The molar ratio of B/Ca was 2.1, although a complete analysis was not successful.

The liquid ammonia extraction procedure was modified by the addition of a second solvent before evaporation. When trimethyl amine was added to the ammonia solution, a white solid precipitated along with the formation of two liquid layers. The solid was approximately 1% calcium borohydride and another product obtained by evaporation of the liquid layers was approximately 10% calcium borohydride (determined polarographically).

Some of the crude products from the bomb were extracted with 0.05 N sodium hydroxide. Sodium borohydride is fairly stable in this medium, and it was thought that perhaps calcium borohydride is also stable. These solutions were polarographed and the identification of the anodic wave obtained as due to the oxidation of borohydride ion is fairly certain.

Rough calculations of the amount present indicated a maximum yield of about 4% of the theoretical amount of borohydride.

Further experiments were made using 99% pure calcium hydride as a starting material. The yields were not increased, although the higher purity of the hydride was probably offset by the larger size of the particles.

Another experimental approach was attempted, using a combustion tube packed with calcium hydride. Gaseous methyl borate carried by a stream of hydrogen could be passed rapidly through the hydride at temperatures higher than those used previously in the bomb. Two runs were made with the temperature held at 425°C. and 485°C., respectively. In each case the volatile products were caught in a series of cold traps and then further fractionated. It was established that in addition to large amounts of excess methyl borate, considerable amounts of acetylene were formed. One of the fractions obtained from the 485°C. run had a vapor pressure of 185 mm. at -109°C. (B_2H_6 has a vapor pressure of 194 mm. at this temperature). An analysis of this material in the mass spectograph failed to show any significant boron peaks. Analyses of other fractions were not completed, and the presence of higher boiling boranes has not been ruled out. However, it is known that methyl borate will undergo numerous cracking reactions in the presence of calcium hydride at these temperatures.

Discussion: On the basis of the experimental work described above, we conclude that calcium borohydride can be prepared by the reaction of methyl borate and calcium hydride. It appears to be stable at room temperature in the solid form as well as in alkaline aqueous solutions. These observations indicate that it has an ionic character similar to sodium borohydride rather than magnesium borohydride. It is insoluble in ether and isopropyl amine and all attempts to separate it in the pure state from solvents such as water and liquid ammonia have resulted in nearly complete decomposition

to calcium borate (except for the very tedious "freeze drying" method reported in the ion exchange section of this report).

We believe that yields of borohydride by pressure bomb technique could be improved by (1) using a more reactive form of calcium hydride, (2) improving the agitation inside the bomb and (3) better methods of extracting and/or identifying the product. None of these obstacles seems insurmountable, and the procedure warrants further investigation.

Investigation of the Conversion of Sodium Borohydride to Calcium Borohydride
by Metathesis and Ion Exchange

Objective: Pure calcium borohydride has not been prepared and its physical and chemical properties could only be estimated by analogy to known borohydrides. A simple preparation from the readily available sodium borohydride and calcium chloride was investigated. The determination of these properties, in particular the solubility in various solvents, would have been useful in other phases of the program.

Summary and Conclusions: The metathesis of calcium borohydride from sodium borohydride and calcium hydride was attempted, using dimethyl formamide, diethyl ether, ethyl alcohol, dioxane, and tetrahydrofuran as solvents; and by ion exchange with water as a solvent. Of the several methods investigated, only the ion exchange method shows promise of producing reasonably pure solid calcium-borohydride. However, the procedure is not economically feasible, the exchange equilibrium is unfavorable, and only small amounts (200-300 mg.) can be prepared at a time. It is possible to produce larger amounts with a larger column, but this would also increase the problem of the decomposition of the borohydride.

Experimental: Sodium borohydride and calcium chloride are insoluble in ether, dioxane, and tetrahydrofuran. Mixtures of the two salts were refluxed in each of these solvents, with the hope that calcium borohydride would be soluble. No product was obtained.

Metathesis in ether was next tried with soluble calcium salts and lithium borohydride. Both calcium bromide (in the presence of lithium bromide) and calcium iodide were used. The products obtained were inactive toward acid and were not identified.

Dimethyl formamide (DMF) has desirable properties for the metathesis reaction. Both sodium borohydride and calcium chloride are soluble, while sodium chloride is only slightly soluble. Anhydrous mixtures of these reactants were prepared in DMF and the sodium chloride removed by centrifuging. Analysis of the filtrate showed that the solute was 90-95% calcium borohydride. The solvent (DMF) was then evaporated under high vacuum, leaving a white solid containing 37% calcium but only 6% borohydride.

The DMF procedure was modified by the addition of a second solvent in order to precipitate the product. Benzene, toluene, meta-xylene, mesitylene, di-n-butyl amine, di-n-amyl amine, diethyl ether, and carbon tetrachloride were tried. Benzene had no effect, even in 60 to 1 excess, and carbon tetrachloride reacted with the borohydride. The other solvents caused a viscous oil to separate, which contained most of the borohydride. It was not possible to separate a solid from this oil. Efforts to produce diborane from this oil and boron trifluoride etherate were unsuccessful.

The ion exchange method carried out in alkaline aqueous solutions was more fruitful. The column was made up in a 100 ml. buret with Dowex-50 AR resin, using an upflow technique. The resin was converted to the calcium form and rinsed with a solution of calcium hydroxide (pH 12). Solutions of sodium borohydride in calcium hydroxide (pH 12) were passed slowly through the column (one drop per second). Under these conditions the exchange of calcium and sodium was at least 90% complete, with little if any decomposition of the borohydride. In this manner solutions containing relatively pure (85%) calcium borohydride were prepared.

The best yields of solid calcium borohydride were obtained by a "freeze-drying" process. The solution was frozen on the inside walls of flasks connected to a vacuum pump. The ice was then sublimed with the

flasks maintained at -5°C . Products were obtained with as much as 78% of the boron present as borohydride. Purification of the product by extraction into other solvents was not successful. Extraction with liquid ammonia yielded a solution containing essentially pure calcium borohydride, but again it was impossible to remove the solvent without decomposition of the product.

Discussion: Although nearly pure solutions of calcium borohydride were prepared in DMF, water, and liquid ammonia, in no case was it possible to isolate a pure solid product. Apparently calcium borohydride forms very strong complexes with the solvent and removal of the solvent involves destruction of the borohydride itself.

The Melting Point and Vapor Pressure of Aluminum Chloride Etherate

Objective: A rough determination of the melting point of aluminum chloride etherate gave a result which was approximately 6°C. higher than previously published values. This fact led to the preparation of pure anhydrous etherate and the accurate determination of its melting point. For a better understanding of its behavior at elevated temperatures, the vapor pressure curve of this compound was also determined.

Summary and Conclusions: Aluminum chloride etherate (prepared by the addition of ether to aluminum chloride at 0°C.) was purified by high vacuum distillation in an all-glass apparatus. The distillate was collected in ampules and sealed off under vacuum. Such precautions were necessary since moisture will attack the etherate readily. Chloride and aluminum analyses agreed with the theoretical values with less than 0.5% errors. The average melting point of several samples and other published values are given in Table I.

The vapor pressure of $\text{AlCl}_3\text{-OEt}_2$ was determined between 94 and 144°C. A distinct change in slope of the vapor pressure curve at 121°C. indicates the point of decomposition. This fact is in agreement with Menzel and Froehlich who observed vapor formation at 120°C.¹

Table I

Melting Point of Aluminum Chloride Etherate

Average obtained by authors	39.4 $\pm$ 0.2°C.
Plotnikov and Kaplan ²	33.0 - 33.8°C.
Gilman and Apperson ³	34°C.
Frankforter and Daniels ⁴	33 - 35°C.

Experimental: An excess of absolute ether (Mallinckrodt Chemical Works, St. Louis, analytical grade) was added slowly to aluminum chloride (Allied Chemical and Dye Corporation, New York, c.p. grade) at 0°C. After filtering the solution, the excess ether was vacuum withdrawn, leaving a brown amorphous solid. A preliminary distillation of this product gave the clear $\text{AlCl}_3\text{-OEt}_2$. This solid was melted and poured rapidly (to have as little hydrolysis as possible) into an all-glass distillation apparatus. The etherate was distilled at a temperature of 65°C. and a pressure of 10^{-2} mm., the distillate being collected in ampules and sealed off under vacuum. Hexagonal plates were obtained when the etherate was allowed to crystallize slowly.

The etherate was analyzed for aluminum by the aluminum oxide method and for chloride by gravimetric silver chloride. The glass ampules containing $\text{AlCl}_3\text{-OEt}_2$ were opened under water to prevent loss of chloride by rapid HCl evolution. The analytical results are summarized in Table II.

Table II

Analytical Results

	<u>Aluminum</u>	<u>Chloride</u>
Average % Found	12.97	51.11
% Theoretical	13.00	51.28
Average % Error	0.23	0.33
Maximum % Error	0.69	0.45

The apparatus used for the determination of the vapor pressure of $\text{AlCl}_3\text{-OEt}_2$ is shown in Figure I. After the etherate was poured into chamber A and sealed at constriction B, a high vacuum of 10^{-4} mm. was established and the mercury in U-tube C was gently degassed with a brush flame. The left mercury tube was sealed off at constriction D while the etherate was kept at -80°C . The etherate was then distilled into U-tube E after a first fraction was collected in tube G, and was sealed off at constriction F. The apparatus was supported in a four-liter beaker together with a thermometer and a three-bladed stirrer. Shell Diallyl oil was used for the oil bath. Heating of the oil bath was done by a variable hot plate and two infrared lamps placed near the side of the four-liter beaker. The mercury heights were measured to within ± 0.05 mm. with a cathetometer.

In order to determine the accuracy of this method, a preliminary run was made with acetophenone and a comparison was made between the vapor pressure curve obtained and literature values. The acetophenone was obtained from Felton Chemical Company Inc., Los Angeles, California. The aliquot used in the determination was a heart cut from a sample which was twice vacuum distilled through a five-foot column using a 56:1 reflux ratio. Table III gives the corrected pressure and temperature measurements for

Figure I

Apparatus for Vapor Pressure Measurement

acetophenone and $\text{AlCl}_3\text{-OEt}_2$. The observed pressures were corrected to 0°C .; stem and calibration corrections were added to the observed temperatures. Figure II is a plot of $\log_{10} p_{\text{mm}}$ versus $1/T$ for acetophenone together with the curves obtained by W. Ham⁵ and G. Kahlbaum.⁶ Figure III is a plot of $\log_{10} p_{\text{mm}}$ versus $1/T$ for $\text{AlCl}_3\text{-OEt}_2$.

Table III

Vapor Pressure-Temperature Measurements for
Acetophenone and Aluminum Chloride Etherate

<u>Acetophenone</u>				<u>Aluminum Chloride Etherate</u>			
Pressure	Temperature	$\log_{10} p_{\text{mm}}$	$10^3/T$	Pressure	Temperature	$\log_{10} p_{\text{mm}}$	$10^3/T$
2.78	54.75	0.444	3.049	1.28	94.64	0.107	2.719
4.41	62.53	0.644	2.979	2.02	99.27	0.305	2.685
7.17	71.57	0.856	2.901	2.95	103.19	0.470	2.657
10.17	78.75	1.007	2.841	6.09	110.52	0.785	2.606
15.23	87.09	1.183	2.776	9.42	115.61	0.974	2.572
18.57	91.43	1.269	2.743	16.13	121.08	1.208	2.536
23.68	96.80	1.374	2.703	20.05	122.93	1.302	2.525
32.55	104.15	1.513	2.650	26.51	125.19	1.423	2.510
40.28	109.21	1.605	2.615	37.08	127.96	1.569	2.493
45.57	112.29	1.659	2.594	52.52	131.44	1.720	2.471
53.63	116.81	1.729	2.564	96.62	138.17	1.985	2.431
62.63	120.27	1.797	2.542	152.87	143.96	2.184	2.397
89.36	129.82	1.951	2.481				
116.64	137.31	2.067	2.436				
154.60	145.58	2.189	2.388

Figure II. Vapor Pressure Curve for Acetophenone.

O, from this investigation; Δ , values of Kohlbaum; $\square$, values of Ham

275 416

Figure III

Vapor Pressure Curve for Aluminum Chloride Etherate

2175 017

Discussion: Figure II shows that there is very close agreement between vapor pressure values obtained in this investigation and those values obtained by Kahlbaum. At lower pressures there are significant differences between our values and those obtained by Ham (approximately 0.07 mm.). These differences are probably a consequence of the decidedly different method used by Ham, whereas the method of Kahlbaum and the method used in this investigation both involve the direct measurement of the height of a mercury column. Because of the close agreement with Kahlbaum and the small deviation from Ham, our method is felt to be satisfactory.

In Figure III there is observed at 121°C. a distinct change in slope of the vapor pressure curve for $\text{AlCl}_3\text{-OEt}_2$. When the apparatus which was used to determine the vapor pressure was allowed to cool to room temperature after the determination, a pressure of about 50 mm. remained, whereas the mercury levels before the determination were at the same height. This indicates that decomposition and not merely dissociation takes place above 121°C., the decomposition point. The best straight line through the first five points in Figure III is given by the following equation.

$$\log_{10} p_{\text{mm}} = - \frac{5965.5}{T} + 16.323$$

Although this equation is experimentally valid only between 94 and 121°C., it is probably a good approximation down as far as 50°C. A calculated value of 0.05 mm. at 65°C. from this equation agrees with the observed behavior of the etherate when it was distilled in the high vacuum apparatus.

References

1. W. Menzel and M. Froehlich, Ber., 75B, 1055 (1942)
2. Plotnikov and Kaplan, C.A., 42, 7151f (1948)
3. H. Gilman and L. Apperson, J. Org. Chem., 4, 162 (1939)
4. G. Frankforter and E. Daniels, J. Am. Chem. Soc., 37, 2560 (1915)
5. W. Ham, J. Franklin Inst., 186, 15 (1918)
6. G. Kahlbaum. Z. physik. Chem., 26, 577 (1898)

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