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Seventh Topical Report

on

THE REACTIONS OF BOROHYDRIDES AND ALUMINOHYDRIDES WITH WOLFRAM (VI) HALIDES

by

Robert W. Bragdon

C&CCC, Y-12
Report's Office, TIC
File 26802
Date 11-12-51

Classification cancelled (or changed to U)
by authority of USAEC HQ
by CO Tan, TISOR, date 5-5-70

Eighth Topical Report

on

PREPARATION AND PROPERTIES OF THORIUM BOROHYDRIDE

by

Robert W. Bragdon

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NEPA Division
Fairchild Engine and Airplane Corporation

NOV 5 1951
C&CCC Y-12
Reports Office
Tech Info Center

Contract SC-2026

November 8, 1950

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9703

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Metal Hydrides - Topical Report

These two reports were prepared by Robert W. Bragdon with the occasional advice of Thomas R. P. Gibb, Jr. and M. Douglas Banus. Density determinations were carried out by Henry W. Kruschwitz, Jr. All members of the staff contributed to some extent in the preparation and purification of starting materials, etc.

We are indebted to Dr. Frank Spedding for a sample of thorium tetrafluoride and to the General Chemical Co. for a cylinder of wolfram hexafluoride.

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Metal Hydrides - Topical Report

Table of Contents

page

Metal Hydrides - Topical Report

Abstract

A comprehensive investigation of methods for the preparation of hydrides of wolfram has been made. A wolfram (IV) hydride-aluminum hydride mixture has been prepared and its N_H and thermal stability determined for its evaluation as a nuclear radiation shield material. Aluminum borohydride has been shown to reduce wolfram (VI) chloride to a subchloride. The alkali borohydrides also reduce hexavalent wolfram, but in no case has a wolfram borohydride been isolated.

Introduction

According to various authorities, the gamma attenuation and neutron moderation characteristics of wolfram coupled with its abundance and high density make it an excellent material for nuclear radiation shields(1). It has the disadvantages of low probability of neutron capture and relatively high secondary gamma production. Boron, with its high-neutron capture and, of course, hydrogen would be desirable additives. Consequently this investigation was undertaken to study likely methods for the preparation of hydrides and borohydrides of the heavy metals.

Historical

The absorption of hydrogen by wolfram metal has been shown to be limited to the formation of a surface film(2-13). While the hydrogen is believed to be present in the ratio of one molecule of hydrogen per two atoms of <u>surface</u> metal, this falls far short of a stoichiometric ratio in massive metal. Even treatment of wolfram with hydrogen in the activated atomic state has failed to produce a hydride(5).

Weichselfelder(14) is widely credited with having prepared a wolfram hydride (WH_3) through the reaction of wolfram hexachloride and phenyl magnesium bromide in an atmosphere of hydrogen. Iron, cobalt, and nickel hydrides were claimed(15-20) to have been prepared in this manner but have not been substantiated by later workers(21, 22). The evidence in support of wolfram hydride formation is based entirely on the measured absorption of hydrogen by an ethereal mixture of wolfram hexachloride and phenyl magnesium bromide. In the case of nickel, it has been demonstrated(17-19) that catalytic hydrogenation of the benzene nucleus can account for sizable hydrogen absorption. To the best of our knowledge, subsequent attempts to prepare wolfram hydride by this method have been unsuccessful(23,24).

The borohydrides are a relatively new class of compounds. The first to be prepared was aluminum borohydride(25) in 1939. Since then this compound has proved a valuable tool in the preparation of other borohydrides when reacted with the metal halides, i.e., uranium(26), thorium, hafnium, zirconium, and titanium borohydrides(27). An attempt(28) was made to prepare the borohydrides of chromium and lead by the reaction of aluminum borohydride with the respective halides, but this resulted

[redacted]

in chromium boride and elemental lead. Diborane has also proved a valuable preparative agent in the synthesis of borohydrides by reaction with the metal alkyls, i.e., aluminum, beryllium(29), lithium(30), and magnesium(31) borohydrides, and by reaction with the methoxides and methoxy borohydrides of sodium(32) and potassium(32). In every instance the borohydrides of the heavy metals have proved to be the most volatile compounds of that oxidation state of the metal. This volatility has offered a convenient means of purification in many cases.

Much less work has been done with the aluminohydrides, no heavy metal aluminohydrides having been reported in the literature. The trimethyl amine addition compound of aluminum hydride was the first to be prepared by Wiberg(33). More recently Schlesinger, Finholt, and Bond(34) have prepared lithium aluminohydride and an aluminum hydride etherate by the reaction of lithium hydride and ethereal aluminum chloride. In a similar manner the aluminohydrides of sodium(35) and calcium(35) have been prepared, although more elaborate techniques have been necessary to obtain good yields and purity.

Lithium aluminohydride has been employed in several previous attempts(36) to prepare other metallic aluminohydrides but has resulted either in the primary hydrides, i.e., SiH_4, GeH_4, SnH_4, AsH_3, SbH_3, MgH_2, and BeH_2, or in the free metals, i.e., Tl and Pb. When the reactions are carried out in diethyl ether and the product sought is precipitated, it is contaminated with lithium chloride. In such cases it is convenient to resort to aluminum hydride which avoids the coprecipitation of a lithium salt.

Discussion of Results

Aluminum borohydride reacts vigorously with wolfram hexachloride at the melting point of the borohydride (-65° C) probably according to the equation:

$$\text{(I)} \quad WCl_6 + Al(BH_4)_3 \dashrightarrow WCl_3 + AlCl_3 + 3/2B_2H_6 + 3/2H_2$$

Simultaneously a portion of the excess aluminum borohydride loses hydrogen to form the non-volatile polymer of the approximate composition AlB_3H_8. The reduction of the wolfram to the trivalent state is demonstrated by the consistent liberation of 1.5 moles of diborane per mole of wolfram. Separation of the aluminum chloride from the solid reaction products by sublimation has further shown that only one mole of aluminum chloride is formed per mole of wolfram. Two moles of aluminum chloride would result if a trivalent wolfram borohydride were formed:

$$\text{(II)} \quad WCl_6 + 2Al(BH_4)_3 \dashrightarrow WB_3H_{12} + 2AlCl_3 + 3/2B_2H_6 + 3/2H_2$$

When the solid products of the wolfram hexachloride-aluminum borohydride reaction are extracted with liquid aluminum borohydride (chosen because it is the only known solvent for the non-volatile polymer AlB_3H_8), a further reduction apparently takes place to an indefinite oxidation state as evidenced by the liberation of more diborane and low recovery of chloride in the leached product. This apparent increased reducing power of liquid over gaseous aluminum borohydride has been observed before in its reaction with chromium chloride(28).

When the hexafluoride of wolfram is used, a more vigorous reaction occurs with considerably more hydrogen evolved. Treatment of the solid portion of the product with methyl alcohol converts boron present as borohydride to methyl borate according to the equation:

$$\text{(III)}\quad BH_4' + 4CH_3OH \qquad B(OCH_3)_3 + CH_3O^- + 4H_2$$

The methyl borate thus formed may then be isolated by distillation together with methyl alcohol and analyzed. Non-labile or boride boron is unreactive and has been shown to be present in the ratio of three to one with the wolfram. The insoluble and non-volatile nature of the aluminum fluoride formed prevents distinguishing between the possible equations:

$$\text{(IV)}\quad WF_6 + 2Al(BH_4)_3 \rightarrow WF_3 + AlF_3 + AlB_3 + 3/2B_2H_6 + 15/2H_2$$

and

$$\text{(V)}\quad WF_6 + 2Al(BH_4)_3 \rightarrow WB_3 + 2AlF_3 + 3/2B_2H_6 + 15/2H_2$$

However, there seems to be no apparent reason why one mole of aluminum borohydride should dehydrogenate as in Equation IV. Such a degree of instability has not been observed in other reactions which result in aluminum fluoride-aluminum borohydride mixtures. Following the reduction of the wolfram hexafluoride to the trivalent state, there is perhaps a metathetical reaction which forms an unstable wolfram borohydride, which in turn decomposes to form a wolfram boride or a mixture of wolfram metal and boron. The reaction of aluminum borohydride with a double salt of trivalent wolfram (such as $NaWF_4$) would be the next logical step, but such compounds are not available to us at the present time.

Diborane apparently has no tendency to react with the wolfram hexahalides for gaseous mixtures with the fluoride can be successfully fractionated. This is in direct contrast to the reactions observed with the analogous aluminum hydride.

Solid lithium borohydride reacts very slowly with wolfram hexachloride at room temperature to liberate diborane and hydrogen. When the temperature of the solid-solid mixture is raised to increase the vapor pressure of the wolfram hexachloride, a violent reaction occurs which liberates approximately one mole of diborane per mole of wolfram. Wolfram hexafluoride with a high vapor pressure at room temperature reacts more readily with lithium borohydride but with the same result. These reactions appear to take place more smoothly when a solvent such as diethyl ether is employed. This has not proved satisfactory, however, because of the contamination of the products with lithium compounds. In no case has there been any positive evidence of the formation of a wolfram borohydride.

Sodium borohydride does not react with either wolfram hexafluoride or hexachloride. Ether does not promote the reaction, while isopropylamine in which sodium borohydride is quite soluble is unsatisfactory because of aminolysis of the wolfram hexahalide.

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When diethyl ether is employed as a solvent, aluminum hydride reacts with wolfram hexachloride to precipitate a wolfram (IV) hydride probably according to the equation:

$$\text{(VI)} \quad WCl_6 + 2AlH_3 \qquad WH_4 + 2AlCl_3 + H_2$$

Because of the tendency of aluminum hydride etherate to form an insoluble polymer, this hydride is contaminated with a variable amount of aluminum hydride. With lithium aluminum hydride, a similar reaction takes place, but in this case lithium chloride is coprecipitated with the wolfram hydride.

Wolfram hexafluoride was also employed in these investigations because of its greater ease of handling in the vacuum line. While the reactions were found to be identical with wolfram hexachloride and helped to determine the course of the reaction, the products were necessarily contaminated with insoluble aluminum fluoride. The reduction of the wolfram to the tetravalent state was inferred from the constant liberation of one mole of hydrogen per mole of wolfram.

The wolfram hydride-aluminum hydride etherate mixture is an extremely pyrophoric white powder which is stable in a vacuum up to about 60° C. The powder density of a sample in which the ratio of aluminum to tungsten was 2.8 was determined by the helium displacement method (H.W.K.) to be 1.3 g/cc. This corresponds to an N_H (including ether hydrogen) of 5.0. These properties are extremely disappointing with relation to the use of wolfram hydride as a shield when compared to the dense material expected.

Experimental

Apparatus - The vacuum line apparatus used for this work has been described by Stock(37), Burg(38), Schlesirger, and Walker(39), and Dorinson(28), and will not be discussed in detail unless a special technique is involved.

Materials

Wolfram Hexachloride - Prepared from wolfram oxide by reduction with hydrogen followed by chlorination and sublimation(40). A. D. MacKay material was used in the early work, but the vacuum sublimation(41) necessary to remove the oxychlorides present proved too arduous. Moderately high purity was indicated by the analyses; wolfram, found 46.3, 44.8%, theory 46.3%; chlorine, found 54.5, 55.2%, theory 53.7%.

Wolfram Hexafluoride - Obtained through the courtesy of General Chemical Co. and purified by distillation in vacuum with condensation at -80° C. Purity was checked by its vapor pressure of 378 mm. at 0° C.

Aluminum Borohydride - Prepared by the reaction of aluminum chloride and sodium borohydride with the volatile impurities removed by passing through a trap cooled to -80° C. The purity was checked by its vapor pressure of 119 mm. at 0° C.

[redacted]

Diborane - Obtained as a by-product in the preparation of aluminum borohydride. The purity was checked by its vapor pressure of 225 mm. at -112° C.

Lithium Borohydride - Commercial product of Metal Hydrides Inc.

Sodium Borohydride - Commercial product of Metal Hydrides Inc.

Aluminum Chloride - Reagent anhydrous Merck.

Lithium Aluminum Hydride - Metal Hydrides Inc. product purified by crystallization from ether-benzene mixture followed by ether extraction. Analysis by hydrogen evolution indicated 99.1% purity.

Aluminum Hydride Etherate - Prepared as a 1% ether solution by the reaction:

$$AlCl_3 + 3LiAlH_4 \qquad 4AlH_3 + \underline{3LiCl}$$ (34)

Diethyl Ether - Commercial anhydrous grade purified by distillation from lithium aluminum hydride in an atmosphere of dry nitrogen.

Isopropylamine - Sharples Chemicals Co. commercial anhydrous material purified by treatment with sodium hydride and distillation from sodium borohydride in an atmosphere of dry nitrogen.

Wolfram Hexafluoride-Aluminum Borohydride Reaction

0.898 m-moles of wolfram hexafluoride (20.1 cc at STP) were condensed on an excess of aluminum borohydride (5.43 m-moles, 121.8 cc at STP) at -196° C. The reaction mixture was warmed to -80° C by replacing the liquid nitrogen bath with a dry ice-acetone bath. At this temperature a violent reaction occurred which blew the black solid product throughout the vacuum line. After remaining in contact with solid for ten hours, the gaseous products were removed and the volume of the mixture measured. The mixture was then passed successively through traps cooled to -112° C, -112° C, and -196° C, and thence through the pumps. The material condensable at -112° C was identified as aluminum borohydride by its vapor pressure of 119 mm at 0° C. The material which passed through the -112° C traps but was condensed at -196° C was identified as diborane by its vapor pressure of 225 mm at -112° C. The non-condensable gas was measured by difference and was assumed to be hydrogen. In this manner 2.54 m-moles of unreacted aluminum borohydride (56.9 cc at STP), 1.375 m-moles of diborane (30.8 cc at STP), and 6.45 m-moles of hydrogen (144.1 cc at STP) were obtained. No wolfram- or fluorine-containing compounds were found among the gaseous products. The proportions of products and reactants in this and subsequent reactions of aluminum borohydride are given in Table VI. For convenience in comparison, all values are related to one m-mole of tungsten.

Metal Hydrides - Topical Report

Wolfram Hexafluoride-Aluminum Borohydride Reaction with Determination of Non-labile Boron Formed

0.924 m-moles of wolfram hexafluoride (20.7 cc at STP) were condensed on an excess of aluminum borohydride (4.83 m-moles, 108.1 cc at STP) at -196° C. The reaction mixture was then warmed slowly in an isopentane bath. At -100° C a slow pressure rise commenced. At -65° C (approximately the melting point of aluminum borohydride), a vigorous reaction occurred which blew the black solid reaction product throughout the vacuum line. The gaseous products were removed, fractionated, and measured. They consisted of 2.40 m-moles (53.8 cc at STP) of unreacted aluminum borohydride, 1.365 m-moles (30.5 cc at STP) of diborane identified by its vapor pressure of 225 mm at -112° C, and an undetermined volume of non-condensable gas.

Methanol was then condensed on the solid reaction products and allowed to react at room temperature. Under these conditions borohydride ions should react according to the equation:

$$\text{(III)} \quad BH_4' + 4CH_3OH \rightarrow B(OCH_3)_3 + CH_3O' + 4H_2$$

A boride or elemental boron would not be expected to react. The methanol together with the methyl borate formed was then distilled to a flask and removed from the vacuum line. The boron was determined after dilution and addition of mannitol by titration with 0.1 N NaOH. A material balance of the boron is presented in Table I.

Table I

Material Balance on Boron in WF_6-$Al(BH_4)_3$ Reaction

B introduced as $Al(BH_4)_3$ = 14.49 m-at. wts.

B recovered as $Al(BH_4)_3$ = 7.20 m-at. wts.

B recovered as B_2H_6 = 2.73* m-at. wts.

B recovered as $(CH_3O)_3B$ = 1.83 m-at. wts.

Total B recovered = 11.76 m-at. wts.

B unrecovered = 2.73* m-at. wts.

2.73 m-at. wts. of non-labile boron remain with 0.924 m-at. wts. of wolfram. On the basis of 1.00 m-at. wts. of wolfram, we have the empirical formula, $W_{1.00}B_{2.96}$.

This non-labile boron is readily explained by assuming the presence of WB_3 in the reaction products which would be formed according to the equation:

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* Note that unrecovered B exactly equals B liberated as diborane. This should be so if diborane arises from decomposition of intermediate $W(BH_4)_6$

$$W(BH_4)_6 \quad WB_3 + 1.5B_2H_6 + 7.5H_2$$

$$\text{(V)}\quad WF_6 + 2Al(BH_4)_3 \rightarrow WB_3 + 2AlF_3 + 3/2B_2H_6 + 15/2H_2$$

but might also be explained by the presence of an aluminum boride as in the hypothetical equation:

$$\text{(IV)}\quad WF_6 + 2Al(BH_4)_3 \rightarrow WF_3 + AlF_3 + AlB_3 + 3/2B_2H_6 + 15/2H_2$$

Wolfram Hexachloride-Aluminum Borohydride Reaction - Aluminum Chloride Sublimation

7.32 m-moles of aluminum borohydride (163.8 cc at STP) were condensed on 1.72 m-moles of wolfram hexachloride at -196° C. The reaction mixture was warmed directly to room temperature and after remaining in contact for four days, the gaseous products were fractionated and measured. 68.7 cc of unreacted aluminum borohydride, 62.9 cc of diborane, and 196.5 cc of hydrogen were obtained. The solid residue was then heated to 100-115° C for 3-4 hrs. and the aluminum chloride sublimate trapped in a U-tube cooled to -80° C. 1.09 m-moles of aluminum chloride were obtained per m-mole of wolfram. This is slightly more than required by the equation:

$$\text{(I)}\quad WCl_6 + Al(BH_4)_3 \rightarrow WCl_3 + AlCl_3 + 3/2B_2H_6 + 3/2H_2$$

but it is to be noted that it is in exact agreement with the slightly high values (approximately 1.63 m-mole) of diborane liberated so that this presence of adsorbed chlorine in the original wolfram hexachloride is suggested. See also the analyses on p 8. The analysis of the residue from the sublimation further confirms the presence of wolfram (III) chloride as demonstrated in Table II.

Table II

Analysis of Product of WCl_6-$Al(BH_4)_3$ Reaction Following Removal of $AlCl_3$ by Sublimation

Element	%	Molar Ratio
W	57.8	1.00
Cl	30.2*	2.71
Al	4.3	0.51
B	7.2	2.11
H	0.5	1.55
Total	100.0	

* By difference since HCl was inadvertently lost during hydrolysis.

Wolfram Hexachloride-Aluminum Borohydride Reaction - Aluminum Borohydride Extraction

2.05 m-moles of wolfram hexachloride were loaded on disc A and side arm B was sealed off. Following evacuations 5.38 m-moles of aluminum borohydride (166.9 cc at STP) were condensed on the sample at -196° C. The reactants were warmed slowly from -112° C to room temperature in a carbon disulfide bath in contact with a volume of sufficient size so that the aluminum borohydride and the diborane formed were in the gaseous phase when the reaction mixture reached room temperature. After remaining in contact for 24 hrs., the gaseous products were fractionated and measured. They consisted of 80.0 cc of diborane, 59.5 cc of unreacted aluminum borohydride, and 149.1 cc of hydrogen (all at STP).

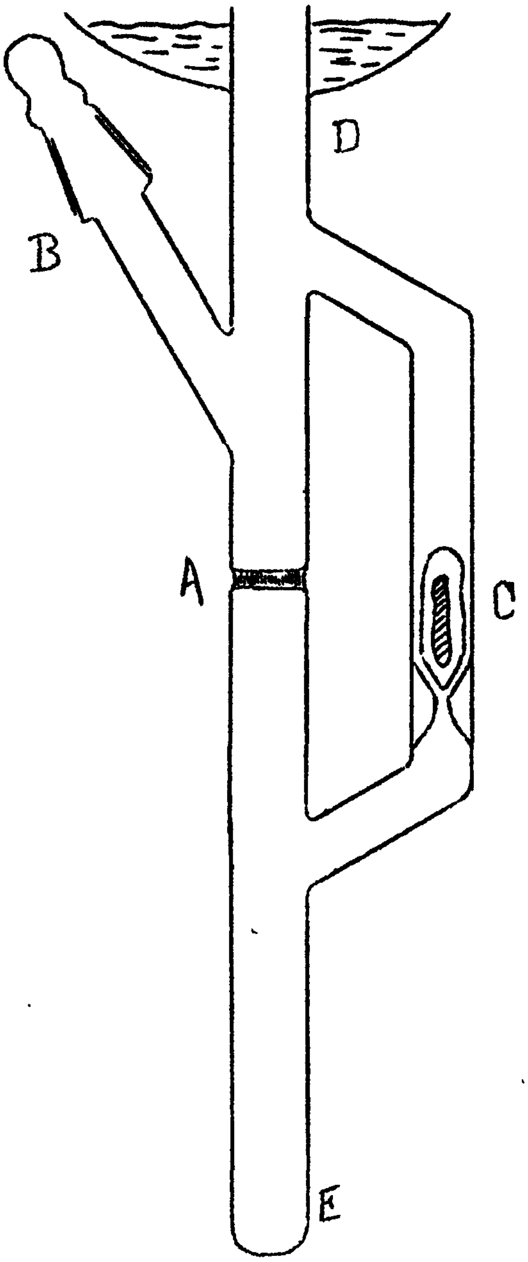
1-2 cc of liquid aluminum borohydride were then condensed at F and continuously refluxed over the residue on the sinter by condensing the liquid with dry ice at D. 25.2 cc of diborane and an undetermined amount of hydrogen were liberated during this step suggesting further reduction of the wolfram. The aluminum borohydride was then pumped off leaving the insoluble product on the sinter A and a non-volatile extract at E. The residue was recovered in an argon-filled dry box and following hydrolysis of a weighed portion on the vacuum line was analyzed completely.

Table III

Analysis of Alide Insoluble Product of WCl_6-$Al(BH_4)_3$ Reaction

Element	%	Molar Ratio
W	50.0	1.00
Cl	13.8	1.43
Al	14.3	1.95
B	16.7	5.68
H	3.66	
Total	98.5	

The total amount of diborane liberated both by the reaction and later during the extraction is 106.2 cc or 4.74 m-moles. On the basis of one m-mole of wolfram, this becomes 2.31 m-moles of diborane per m-mole wolfram and corresponds to a reduction in the valence of the wolfram to 1.38 (possibly a mixture of lower valence chlorides and free metal) which is in good agreement with the value of 1.43 to be seen in Table III. It is to be assumed that the reduction is carried further because of the presence of liquid alide.



CONTINUOUS
VACUUM LINE
EXTRACTION TUBE

A. Sintered glass disc
B. Loading side arm
C. Magnetically controlled valve
D. Dry ice condenser
E. Tube for collection of Soluble materials

Fig I

Wolfram Hexachloride-Aluminum Borohydride Reaction - Benzene and Ether Extraction

A reaction was carried out in the usual manner and the residue extracted with benzene and ether under argon. Confusing results were obtained as evidenced by the analyses appearing in Table IV.

Table IV

Analysis of Benzene-Ether Insoluble Solid Product of

WCl_6-$Al(BH_4)_3$ Reaction

Element	%	Molar Ratio
W	47.7	1.00
Cl	12.7	1.38
Al	24.1	3.45
B	2.4	0.82
H	1.7	6.52
C	6.0	1.93
Total	94.6	

The boron analysis is suspected to be incorrect (low), since it was done early in the investigation when the technique had not been perfected. The low chloride analysis is not easily explained. It may be that deviation from vacuum line techniques is responsible.

Table V

Proportions of Reactants and Products in Aluminum Borohydride-Wolfram Hexahalide Reactions

No.	Halide	$\frac{\text{Alide}}{W}$	$\frac{B_2H_6}{W}$	$\frac{H_2}{W}$	$\frac{AlX_3}{W}$	$\frac{H_2}{\text{Alide}}$	Calculated Comp. of Polymer
1	WF_6	3.23	1.49	7.19		2.23	$AlB_3H_{7.0}$
2	WF_6	2.63	1.48				
3	WCl_6	2.69	1.97	2.63		0.98	$AlB_3H_{9.0}$
4	WCl_6	2.05	1.58	2.95	ca. 1.00	1.44	$AlB_3H_{8.8}$
5	WCl_6	1.94	1.62	2.71		1.40	$AlB_3H_{8.7}$
6	WCl_6	2.00	1.63	2.97		1.49	$AlB_3H_{8.4}$
7	WCl_6	2.47	1.63	5.10	1.09	2.06	$AlB_3H_{7.9}$
8	WCl_6	2.34	1.76	3.25		1.39	$AlB_3H_{8.3}$

Wolfram Hexafluoride-Diborane Reaction

No experiment was attempted which was designed primarily to investigate a reaction between wolfram hexafluoride and diborane. A reaction of wolfram hexafluoride with lithium borohydride, however, resulted in a gaseous mixture of wolfram hexafluoride and diborane which showed no tendency to react at room temperature and could be separated by careful fractionation.

Wolfram Hexafluoride-Lithium Borohydride Reaction

1.345 m-moles of wolfram hexafluoride (30.1 cc at STP) were condensed on 65.4 m-moles of powdered lithium borohydride (1.50 g of 95% material) at -196° C in a tube fitted with a magnetic seal(27) and the tube sealed off under vacuum. After a three-day reaction period at room temperature, the tube was connected to the line and opened. A large amount of non-condensable gas, probably hydrogen, was pumped off. 1.17 m-moles of diborane (26.2 cc at STP), identified by a molecular weight determination of 27.9, were collected in a liquid nitrogen trap. When ether was condensed on the solid residue, evolution of non-condensables and a black suspension resulted. There was no volatile wolfram compound formed.

Wolfram Hexachloride-Lithium Borohydride Reaction

1.39 m-moles of wolfram hexachloride (0.553 g) were mixed with 69.7 m-moles of powdered lithium borohydride (1.90 g) in a 50 cc round-bottom flask. The flask was attached to the vacuum line by a 19/38 joint and the mixture pumped on at room temperature for eight hours.

About 3 cc of diborane were collected in a liquid nitrogen trap during this period. Since the vapor pressure of wolfram hexachloride is apparently too low for appreciable reaction at room temperature, the mixture was heated. At 100° C a sudden violent reaction occurred which dusted the powder throughout the line. A total of 1.33 m-moles of diborane (29.8 cc at STP) were collected.

Wolfram Hexafluoride-Lithium Hydride Reaction

Ether was condensed on a mixture of 2.12 m-moles of wolfram hexafluoride and 245 m-moles of lithium hydride (-100 mesh, 95%) in a 50 cc flask attached to the vacuum line. The mixture was warmed to room temperature and stirred overnight with a magnetic bug. No evolution of hydrogen was noted. The mixture was then filtered under nitrogen and the clear filtrate evaporated on the vacuum line. A greenish-white residue resulted which was apparently an etherate of wolfram hexafluoride.

Wolfram Hexafluoride-Sodium Borohydride Reaction

0.77 m-moles of wolfram hexafluoride (17.3 cc at STP) were condensed on 90 m-moles (97.0% by hydrolysis analysis) of powdered sodium borohydride in a tube fitted with a seal-off constriction and a magnetic seal. The tube was sealed off under vacuum and left at room temperature with occasional agitation for one week. On opening it was found that no pressure of hydrogen had been developed and about 85% of the wolfram hexafluoride was recovered. The residue was then heated to 150° C in vacuum in a Washburn-type molecular still. No distillation occurred.

Wolfram Hexachloride-Sodium Borohydride Reaction

Ether was condensed on a mixture of wolfram hexachloride (0.2 g) and sodium borohydride (1.0 g) at -196° C and the mixture warmed to room temperature and stirred for four hours. No evolution of diborane or hydrogen was noted. Following filtration under nitrogen, the wolfram hexachloride was recovered from the filtrate unchanged.

Wolfram Hexachloride-Sodium Borohydride Reaction in Isopropylamine

An isopropylamine solution containing 37.2 m-moles of sodium borohydride was added to 2.36 m-moles of solid wolfram hexachloride at 0° C in an atmosphere of argon. An initial vigorous reaction resulted as evidenced by the rapid evolution of about 50 cc of gas. A fine white precipitate formed after the initial reaction had subsided leaving a dark red-brown solution. The mixture was centrifuged under argon and the clear filtrate evaporated to dryness on the vacuum line. The residue was extracted with ether to remove the insoluble excess of sodium borohydride. The solution was centrifuged and dried on the vacuum line. On heating to remove the last traces of ether, sublimation of a white crystalline material took place between 50-70° C. Chemical analysis showed this sublimate to be an isopropylamine-borine addition compound, $(CH_3)_2CHNH_2BH_{3x}$. Boron theoretical 14.9%, found 16.2%; nitrogen theoretical 19.2%, found 18.8%; carbon theoretical 49.4%, found 51.0%; hydrogen theoretical 16.6%, found 16.4%.

An isopropylamine solution of 6.24 m-moles of wolfram hexachloride (2.48 g) was added to an isopropylamine solution of 128 m-moles of sodium borohydride (5.00 g) in an atmosphere of argon. The solution was filtered and dried on the vacuum line. The residue was extracted with ether and this solution filtered and dried on the vacuum line by pumping for several hours at room temperature and then at 60° C with loss of a non-condensable gas. The complete analysis of the glassy brown residue appears in Table VI.

Table VI

Analysis of Ether-Soluble Product of $NaBH_4-WCl_6$ Reaction

Element	%	Molar Ratio
W	35.5	1.00
B	11.1	5.32
N	8.7	3.23
C	27.8	12.0
H	7.73	39.8
Cl	0.1	
Na	3.55	0.8
O (calc.)	1.8	0.6
Total	96.3	

Density = 1.98/cc (H.W.K.)

A sample of this material was pyrolyzed at 600° C in vacuum. An analysis of the residue appears in Table VII.

Table VII

Analysis of Pyrolyzed Ether-Insoluble Residue of $NaBH_4-WCl_6$

Element	%
W	50.5*
B	23.1
N	2.9
C	4.5
H	0.4
Na	5.1*
Total	86.5

Density = 3.23 g/cc (H.W.K.)

* calculated

Reaction of Wolfram Hexafluoride with Aluminum Hydride

The reaction tube in which this preparation was made is illustrated in Fig. (2). 51.1 g of an 0.648% solution of aluminum hydride in ether (11.05 m-moles) were weighed into flask A and the apparatus assembled on the vacuum line. After degassing and evacuation with the hydride solution cooled to -196° C in liquid nitrogen, 19.20 cc of wolfram hexafluoride (0.857 m-moles) were condensed on the hydride. The mixture was then warmed slowly to -80° C and stirred intermittently with a magnetic stirrer. 16.0 cc of hydrogen were liberated at this temperature. On warming to 0° C, 3.8 cc more of hydrogen were liberated giving a total of 19.8 cc of hydrogen (0.885 m-moles).

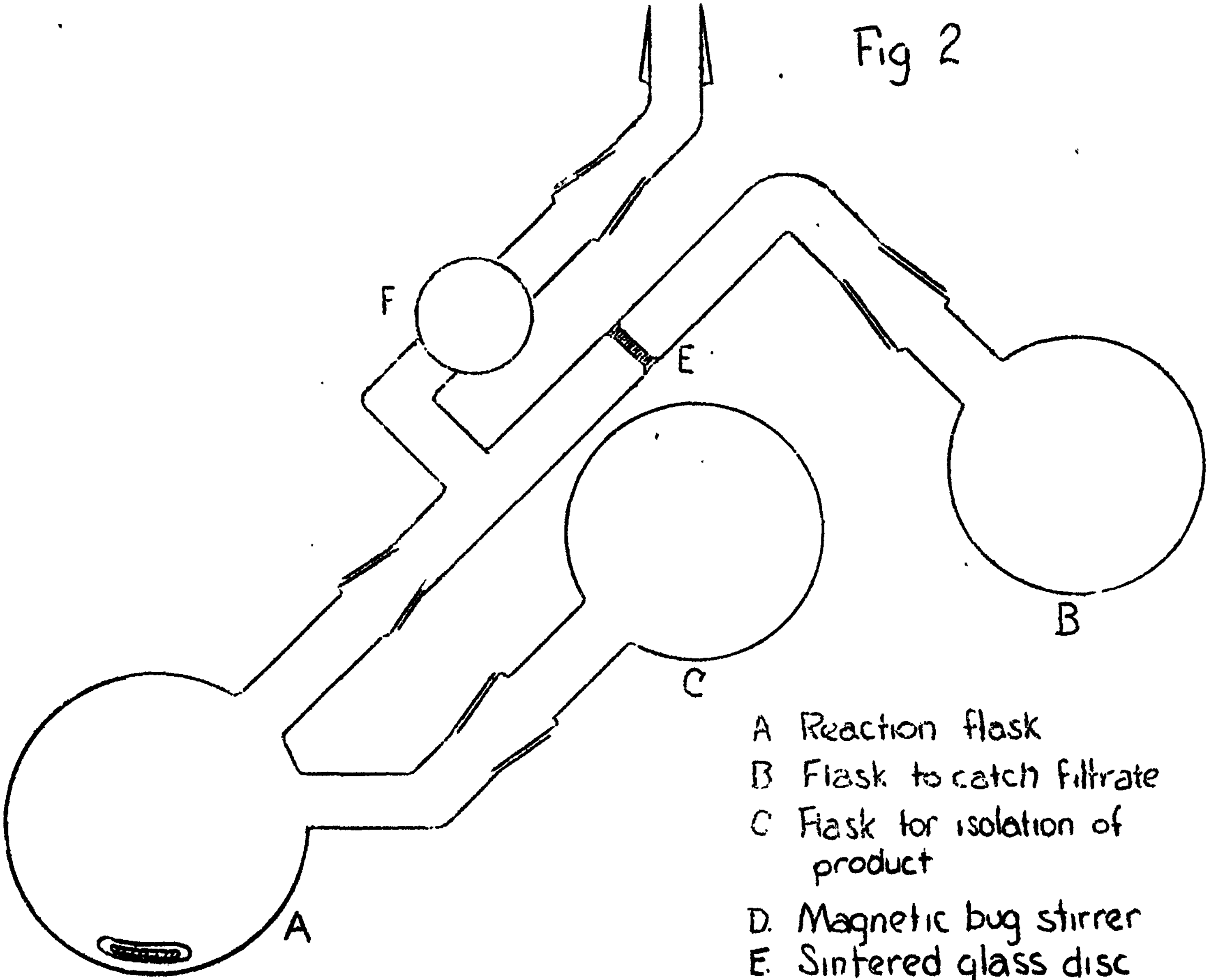
The molar ratio of hydrogen liberated to wolfram hexafluoride used was, therefore, 1.04, indicating a reduction in the valence of the wolfram to the tetravalent state.

The reaction mixture was then warmed to room temperature and stopcock F closed. The reaction tube was removed from the line and flask B cooled in ice water. The reaction mixture was force filtered by its own vapor pressure into flask B. The precipitate was then washed four times with 50 cc portions of ether distilled from the filtrate in B.

The reaction tube was joined to the line again and the precipitate dried in vacuum at 55° C for ninety minutes and transferred under dry nitrogen to flask C by inverting the reaction tube. Flask C was transferred directly to the line while under an atmosphere of dry nitrogen. The dried sample was then hydrolyzed by condensing first dioxane and the water on the sample and the hydrogen liberated measured by pressure developed in a calibrated volume of the line. Correction was made for the vapor pressure of the solution which was experimentally determined.

The wolfram content was determined by precipitation with cinchonine reagent and ignition to the oxide. Aluminum was determined by precipitation as the 8-hydroxy quinolate and dried and weighed as such. The fluorine was titrated with thorium nitrate to the zirconium alizarin-lake end point after separation by distillation as fluosilic acid. A complete material balance is contained in Table VIII.

Fig 2



A Reaction flask
B Flask to catch filtrate
C Flask for isolation of product
D. Magnetic bug stirrer
E. Sintered glass disc
F. Stopcock

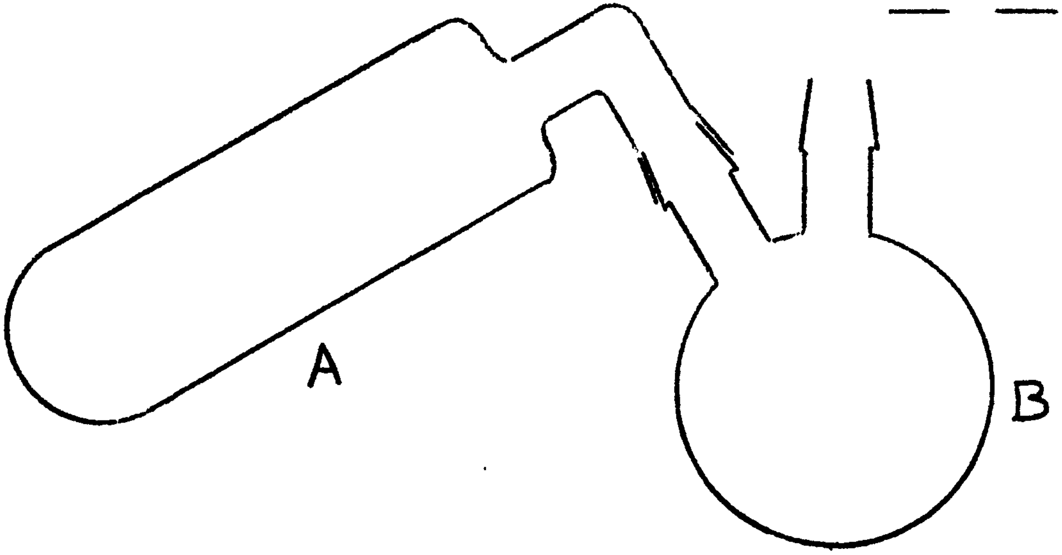


Fig 3

Table VIII

Material Balance in WF_6-AlH_3 Reaction

Material	W g	Al g	H cc	F g
Product	0.1100	0.0648	147	0.0625
Product on walls	0.0429	0.0253	57	0.0244
Filtrate		0.2000	501	
Filtrate on walls		0.0241	60	
Gas evolved			40	
Totals found	0.1529	0.3142	805	0.0869
Totals used	0.1574	0.2980	781	0.0976

The empirical formula of the product is $W_{1.00}Al_{4.02}H_{10.97}F_{5.50}$. Assuming the fluoride to be present as ether-insoluble aluminum fluoride, we obtain by subtraction, $W_{1.00}Al_{2.19}H_{10.97}$. In turn assuming the aluminum to be present as aluminum hydride polymer, we obtain by subtraction, $W_{1.00}H_{4.4}$. Considering the analytical difficulties involved, this is reasonably close to the tetravalent hydride dictated by the hydrogen evolution during reaction.

In calculating the hydrogen content expressed above in the empirical formula, the assumption was made that any wolfram-hydrogen bond would be hydrolyzed according to the reaction:

$$\text{(VII)} \quad WH_4 + 2H_2O \longrightarrow WO_2 + 4H_2$$

Our investigations have not been extensive enough to establish this as a fact, and it should be mentioned that iron, cobalt, and nickel hydrides are supposed to be decomposed catalytically by water according to the equation:

$$\text{(VIII)} \quad MH_2 + H_2O \longrightarrow M + H_2$$

Nevertheless the good hydrogen material balance obtained seems to support the first equation.

Reaction of Wolfram Hexachloride with Aluminum Hydride

(A) 46.4 g of a 0.893% ether solution of aluminum hydride (13.8 m-moles) were placed in flask A of reaction tube in Fig. (2). 0.243 g of sublimed wolfram hexachloride (0.612 m-moles) were placed in flask B and the apparatus assembled on the vacuum line. After degassing and evacuation about 50 cc of ether were condensed on the wolfram hexachloride. The solution was filtered in a partial atmosphere of nitrogen (to prevent bumping) onto the aluminum hydride solution at a temperature of -196° C and the nitrogen pumped off. A cherry red precipitate formed which turned white on warming to 0° C. 17 cc of hydrogen (0.76 m-moles) were evolved making the H_2/WCl_6 ratio = 1.24.

The reaction mixture was filtered into flask B and the precipitate washed four times with 50 cc portions of ether distilled from the filtrate. The dried product was transferred in flask C directly to the vacuum line and hydrolyzed as above. Analysis yielded the empirical formula, $W_{1.00}Al_{5.00}H_{18.3}Cl_{0.14}$. Assuming the chloride to be present as the by-product aluminum chloride and subtracting $Al_{0.05}Cl_{0.14}$ gave $W_{1.00}Al_{4.95}H_{18.3}$. Furthermore assuming the remaining aluminum to be present as aluminum hydride polymer and subtracting $Al_{4.95}H_{14.85}$ yielded $W_{1.00}H_{3.45}$.

(B) 50.8 g of a 0.756% ether solution of aluminum hydride (12.82 m-moles) were placed in flask A of the reaction tube in Fig. (2). 0.329 g of wolfram hexachloride was placed in flask B and the apparatus assembled on the vacuum line. After degassing and evacuation, about 50 cc of ether were condensed on the wolfram hexachloride. Solution was not complete, and it was decided not to measure the hydrogen evolved in the reaction. The solution was filtered onto the aluminum hydride at a temperature of -196° C. The cherry red precipitate turned white on warming to 0° C.

The reaction mixture was filtered and washed as above. After transfer in flask C to the vacuum line, the product was pyrolyzed in vacuum by heating slowly to 200° C. The hydrogen pressure developed in a calibrated volume was measured and corrected for the presence of ether vapor arising from the residual ether in the dried product. Water was then condensed on the pyrolyzed material to prevent a fire when it was removed from the line. Analysis yielded the empirical formula, $W_{1.00}Al_{3.19}H_{11.84}Cl_{0.78}$. Subtraction of $Al_{0.26}Cl_{0.78}$ gives $W_{1.00}Al_{2.93}H_{11.82}$ which may be assumed to be $W_{1.00}H_{3.03}$ and $Al_{2.93}H_{8.79}$.

Hydrogen Liberated During Reaction of Aluminohydrides with Wolfram Hexachlorides

The molar ratios of hydrogen evolved to wolfram hexahalide used have already been reported in two instances. To substantiate further the presence of tetravalent wolfram in the ether-insoluble products, a series of experiments were carried out in which the hydrogen evolution was measured, but no attempt was made to separate and analyze the other products.

In the reaction in which wolfram hexafluoride was employed, a large excess of 1% ether solution of aluminum hydride or lithium aluminum hydride was placed in reaction tube of A of Fig. (1). After evacuation and degassing, a known amount of the fluoride was condensed on the sample. The hydrogen evolution was first noted at -80° C where the low vapor pressure of ether permitted a direct measurement of hydrogen pressure. The reactions at this temperature proved to be variable and incomplete. The hydrogen pressures developed on warming to 0° C were corrected for the vapor pressure of ether. It was necessary to determine the amount of ether vapor in the gaseous phase experimentally because of the reluctance of the ether to come to equilibrium in the presence of the noncondensable gas. The gaseous phase was pumped through a trap cooled with liquid nitrogen and the ether collected and measured separately.

The reactions of wolfram hexachloride were carried out in reaction tube B of Fig. (3). The chloride was added as a solid from the side arm. The molar ratios are to be found in Table IX.

Table IX

Hydrogen Liberated by Reactions WX_6-AlH_3 and WX_6-$LiAlH_4$

No.	Hydride	Halide	H_2/WX_6
1	$LiAlH_4$	WF_6	0.85*
2	$LiAlH_4$	WF_6	0.83*
3	$LiAlH_4$	WF_6	1.09
4	AlH_3	WF_6	1.07
5	AlH_3	WF_6	1.04
6	AlH_3	WCl_6	1.24
7	AlH_3	WCl_6	0.98
8	$LiAlH_4$	WCl_6	1.11

* At -80° C.

These results demonstrate clearly that one mole of hydrogen is liberated per mole of wolfram. Furthermore it has been observed by us that the ratios of aluminum to wolfram and chloride to wolfram are seldom as high as four. There is, therefore, some evidence to support the equation:

$$\text{(VI)} \quad WX_6 + 2AlH_3 \rightarrow WH_4 + 2AlX_3 + H_2$$

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Metal Hydrides - Topical Report

Summary

(1) Aluminum borohydride reduces wolfram (VI) chloride to wolfram (III) chloride, but the latter does not react further to form a wolfram borohydride.

(2) Alkali metal borohydrides reduce the wolfram hexahalides to the tri- or tetravalent state. There being no obvious method for freeing the product of alkali chlorides, this method was given only cursory attention.

(3) Aluminum hydride etherate ($AlH_3.1/3Et_2O$) reacts with wolfram hexachloride and wolfram hexafluoride to form a wolfram (IV) hydride-aluminum hydride mixture.

(4) The low density, thermal instability, and pyrophoric nature of the wolfram hydride-aluminum hydride mixture militate against its use as a nuclear radiation shield.

(5) The reaction of aluminum borohydride with $NaWF_4$ is suggested as the logical approach to the preparation of wolfram borohydride.

Metal Hydrides - Topical Report

Bibliography

(1) Ohlinger, L. A., Nucleonics 5, No. 4, 4-15 (1949).

(2) Sieverts, A. and Bergner, E., Ber. Deutsch. chem. Ges. 44, 2394-2402 (1911)S.

(3) Blodgett, K. B., and Langmuir, I., Phys. Rev. 40, 78-104 (1932).

(4) Frankenburg, W. and Hodler, A., Trans. Faraday Soc. 28, 299 (1932).

(5) Pietsch, Z., Elektrochem. 39, 585 (1933).

(6) Roberts, J. K. and Whipp, B., Proc. Cambridge Phil. Soc. 30, Pt.3, 376-9 (1934).

(7) Frankenburg and Hodler, A., Naturwissenschaften 23, 609 (1935).

(8) Roberts, J. K., Proc. Roy. Soc. London A, 152, 445 (1935).

(9) Roberts, J. K., Proc. Phil. Soc. 32, 152-7 (1936).

(10) Roberts, J. K., Proc. Roy. Soc. London A, 161, 141 (1937).

(11) Frankenburg, W. G., J. Am. Chem. Soc. 66, 1827-38 (1944).

(12) Frankenburg, W. G., J. Am. Chem. Soc. 66, 1838-49 (1944).

(13) Halsey, G. and Taylor, H. S., J. Chem. Physics 15, 624 (1947).

(14) Weichselfelder, T. and Thiede, B., Ann. 447, 64 (1926).

(15) Schlenk, W. and Weichselfelder, T., Ber. 56B, 2230-4 (1923).

(16) Weichselfelder, T. and Kossodo, Ber. 62B, 769-71 (1929).

(17) Balandin, A. A. et al, J. Gen. Chem. (U.S.S.R.) 11, 577-89 (1941).

(18) Balandin, A. A., et al, Acta Phys. U.R.S.S. 18, 300-10 (1943).

(19) Balandin, A. A., et al, Acta Phys. U.R.S.S. 18, 157-166 (1943).

(20) Ray, R. C. and Sahai, R. B. N., J. Indian Chem. Soc. 20, 213-17 (1943); 23, 61-6 (1946); 23, 67-72 (1946).

(21) Schmidt, O., Z. physik. Chem. 118, 193-239 (1925) et seq.

(22) Banus, M. D. and Gibb, T. R. P., Jr., Topical Report No. 3.

(23) Progress Report of NEPA Group at Iowa State College, June 20 - July 20, 1948 NEPA-ISC-4, NEPA 695-IS-4; July 20 - August 20, 1948 NEPA-ISC-5, NEPA 744-IS-5.

(24) Progress Report Nos. 11 and 13, Metal Hydrides Incorporated.

(25) Schlesinger, H. I., Sanderson, R. T., and Burg, A. B., J. Am. Chem. Soc. 61, 536 (1939); 62, 3421 (1940).

(26) Schlesinger, H. I. and Brown, H. C., to be published.

(27) Hoekstra, H. R. and Katz, J. J., J. Am. Chem. Soc. 71, 2488 (1949).

(28) Dorinson, A., Ph.D. Thesis, University of Chicago, 1946.

(29) Burg, A. B. and Schlesinger, H. I., J. Am. Chem. Soc. 62, 3425 (1940).

(30) Schlesinger, H. I. and Brown, H. C., J. Am. Chem. Soc. 62, 3429 (1940).

(31) Schlesinger, H. I. et al, U. S. Navy Report 1945, Contract No'S N173 s-9058, s-9820.

(32) Hoekstra, H. R., Ph.D. Thesis, Univ. of Chicago, 1947.

(33) Wiberg, E. and Stecker, O., Ber. 75, 2003-12 (1942).

(34) Finholt, A. E., Bond, A. C., Jr. and Schlesinger, H. I., J. Am. Chem. Soc. 69, 1199-1203 (1949).

(35) Schlesinger, H. I. et al, U. S. Navy Report, 1947, Contract No. N6Ori-20.

(36) Schlesinger, H. I., et al, U. S. Navy Reports.

(37) Stock, A., "Hydrides of Boron and Silicon" Cornell University Press, Ithaca, N. Y., 1933.

(38) Burg, A. B., J. Am. Chem. Soc. 56, 499 (1934).

(39) Schlesinger, H. I. and Walker, A. O., J. Am. Chem. Soc. 57, 622 (1935).

(40) Lietzke, M. H., and Holt, M. L., Inorganic Syntheses III, pp 163-166, McGraw-Hill Book Co., Inc., N. Y. (1950).

(41) Ketelaar, Oosterhaut, and Braun, Rec. trav. chim. 62, 597-605 (1943).

Eighth Topical Report

on

PREPARATION AND PROPERTIES OF THORIUM BOROHYDRIDE

by

Robert W. Bragdon

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Metal Hydrides - Topical Report

Table of Contents

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Metal Hydrides - Topical Report

Abstract

An investigation of the chemical and physical properties of thorium borohydride, which pertain to its use as a low-temperature nuclear radiation shield, is presented. Values are taken from the literature when available and are supplemented where necessary by our experimental investigation.

Introduction

Thorium borohydride is one of the few heavy metal borohydrides which showed promise of possessing the thermal stability, low volatility, and high hydrogen density (sixteen hydrogen atoms per thorium atom) required in a nuclear radiation shield material.

Both boron and hydrogen have desirable shielding characteristics, and the atomic per cent of these elements in this compound is higher than in any other reported borohydride of comparable thermal stability. This work was undertaken to obtain more information about this compound and also as a basis for the evaluation of other possible heavy metal borohydrides as shield materials.

Historical

The first heavy metal borohydride to be prepared was uranium borohydride(1) according to the equation:

$$\text{(I)}\quad UF_4 + 2Al(BH_4)_3 \longrightarrow U(BH_4)_4 + 2AlF_2BH_4$$

Subsequently the borohydrides of thorium, hafnium, zirconium, and titanium were prepared(2) similarly.

Discussion

Preparation of Thorium Borohydride

The only known method for preparing thorium borohydride at the present is by the reaction of aluminum borohydride and thorium tetrafluoride at room temperature. The reaction proceeds without violence to give yields of 80%. The product is easily separated and purified by sublimation in vacuum from the reaction mixture. Chemical analysis shows the product to be 98-100% pure. The danger involved in handling aluminum borohydride is the only disadvantage to this method of preparation. The demand for large amounts of thorium borohydride would justify an investigation of other means of preparation such as metathetical reactions of alkali borohydrides with thorium tetrahalide in suitable solvents.

Vapor Tension

Hoekstra and Katz have measured the vapor tensions of thorium borohydride at 130° C and 150° C and reported(2) them to be 0.05_{mm} and

(1) Schlesinger, H. I. and Brown, H. C., to be published.

(2) Hoekstra, H. R. and Katz, J. J., J. Am. Chem. Soc. 71, 2488 (1949).

0.20$_{mm}$ respectively.

Melting Point

Thorium borohydride has a reported(2) melting point of 203-204° C (with decomposition). We have been unable to confirm this having observed no melting as high as 240° C whether the sample was heated with the oil bath or the oil bath preheated and the sample plunged in.

X-Ray Investigation

W. H. Zachariasen(2) showed it to be isomorphous with uranium borohydride.

Solubilities

Thorium borohydride is insoluble in benzene(2), tetralin, n-heptane, and triethylamine. It is soluble to the extent of 23.6 g/100 g solvent in tetrahydrofuran(2) and to the extent of 47.0 g/100 g solvent in diethyl ether(2) with which it forms a stable etherate.

Density

The powder density of two separate preparations was determined by one of us (H.W.K.) to be 2.59 ± .02 g/cc at room temperature by the helium displacement method.

Hydrogen Density

The theoretical N_H of thorium borohydride may be calculated knowing the density, molecular weight, and number of hydrogen atoms per molecule.

$$N_H = \frac{16 \times 2.59 \times 60.6}{291.5} = 8.62$$

Thermal Stability

Thorium borohydride is stable indefinitely at 150° C in an atmosphere of hydrogen. At 160° C it decomposes irreversibly at the rate of 0.01% per hour to liberate hydrogen.

Stability in Air

Thorium borohydride appears to be intermediate between lithium borohydride and lithium aluminohydride in its rate of decomposition in moist air (see Fig. (1)). It does not spontaneously inflame at room temperature.

Ignition Temperature

Thorium borohydride will ignite when crushed on a metal surface heated to 160° C. It has not been observed to ignite at lower temperatures.

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Metal Hydrides - Topical Report

Casting

Our inability to melt thorium borohydride either in a vacuum or under an atmosphere of hydrogen has prevented the casting of a pellet. The stability of the material in air suggests that a pellet could be pressed from the powder by standard methods.

Experimental

Typical Preparation of Thorium Borohydride

A sample of anhydrous thorium tetrafluoride 4.075 g. was added through a side arm to a 50 cc bulb attached to a vacuum line. The side arm was sealed off and the bulb evacuated and flamed. An excess of aluminum borohydride was condensed on the sample and the reaction bulb isolated from the line by means of a mercury float valve. The sample was stirred by means of a magnetic bug for four days at room temperature. The stirring was necessary to prevent caking of the solids and consequent lack of contact between the reactants. After this period the unreacted aluminum borohydride was pumped off and stored. The reaction tube was then heated to 150° C by means of a hot air bath while maintaining continuous evacuation. Aluminum borohydride arising from the disproportionation of aluminum fluoro borohydrides was pumped away and thorium borohydride sublimed and condensed above the heated zone where it was prevented from falling back by an inner seal collar in the neck of the 50 cc bulb. 2.96 g. of product were obtained corresponding to a yield of 77%.

A portion of the product was transferred in an argon-filled dry box to 500 cc hydrolysis bulb. The bulb was attached to the vacuum line by means of a 19/38 ground glass joint and evacuated. An excess of water was condensed on the sample at -80° C and the mixture warmed to room temperature. The hydrogen pressure developed in a known volume was corrected for water vapor pressure and the per cent hydrogen in the thorium borohydride calculated from the equation:

$$\text{(II)}\quad BH_4^- + 2H_2O \longrightarrow BO_2^- + 4H_2$$

Boron was separated from the solution and precipitated solids by distillation as methyl borate and was determined by titration of the liberated boric acid in the presence of mannitol. Thorium was put into solution by means of a sugar charcoal-peroxide fusion and precipitated successively with ammonia, hydrofluoric acid, and ammonia, and was weighed as the oxide. Thorium, found 80.9%, theory 79.6%; boron, found 15.0%, theory 14.85%; hydrogen, found 5.41%, theory 5.52%.

Melting Point

A sample of thorium borohydride was placed in a tube fitted with a thermocouple well and a 19/38 ground glass inner joint. The tube was attached to the vacuum line, evacuated, and a pressure of slightly less than one atmosphere of hydrogen was introduced. The tube was then heated in an oil-filled Thiele tube to its reported melting point (203-204° C). When no fusion took place at this point, the

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temperature was slowly raised to 236° C. There was no melting. The tube was then cooled to room temperature and the decomposition calculated from the pressure increase in the calibrated volume. Decomposition ($H_2\uparrow$) had occurred to the extent of 5.6%.

It was feared that decomposition during heating might have contaminated the hydride to the extent that it would not melt. Consequently small samples were sealed in capillary melting point tubes under vacuum. These tubes were plunged into the previously heated oil bath at the desired temperatures. No evidence of melting was observed as high as 240° C.

Solubilities

N-heptane, tetralin, and triethylamine were condensed on 0.1-.2 g. samples of thorium borohydride in centrifuge tubes attached to the vacuum line by ground glass joints. The solvents were shaken intermittently with the hydride at room temperature for 24 hrs. Aliquots of the clear solvents were pipetted, hydrolyzed, and analyzed for thorium. No detectable solubility was observed in any case.

Density

The densities of two powdered samples were determined (H.W.K.) by the helium displacement method in an apparatus described(3) by Schumb and Rittner. Values of 2.58 and 2.61 g/cc were obtained. The average value of 2.59^5 ± .02 g/cc was taken.

Thermal Stability

A 0.3 g. sample of thorium borohydride was sealed off under a pressure of hydrogen (88.9 cm Hg) in a tube fitted with a mercury-filled manometer. The outer end of the manometer was open to the atmosphere. A pledget of glass wool was situated directly over the sample to aid in preventing sublimation. The portion of the tube containing the hydride was then immersed in an oil bath heated electrically and controlled by a DeKhotinsky thermoregulator. The thorium borohydride was maintained at a temperature of 150° C for 144 hrs. with less than 0.1% decomposition and no sublimation. At 160° C the sample decomposed at the steady rate of 0.03 mg per hour (.01% per hour) for as long as the experiment could be continued (35 hrs.). Considerable sublimation occurred at this temperature despite the initial pressure of hydrogen and the pledget of glass wool.

Stability in Air

0.2337 g. of thorium borohydride were weighed into a tared 50 cc beaker and exposed to moist air (50% relative humidity). The loss of active hydrogen was calculated by the gain in weight from the equation:

$$\text{(III)}\quad Th(BH_4)_4 + 8H_2O \longrightarrow Th(BO_2)_4 + 16H_2$$

The gain in weight over an extended length of time showed that a hydrate of thorium borate was probably formed but this was assumed not to happen until all active hydrogen was lost (see Fig. (1)).

When it was observed that thorium borohydride did not inflame spontaneously at room temperature, it was decided to determine the ignition temperature. Small crystals of this material were crushed on an aluminum block previously heated to the desired temperature. The lowest temperature at which the material flashed was 160° C.

Summary

(1) The procedure of Hoekstra and Katz for the preparation of thorium borohydride has been checked and found satisfactory.

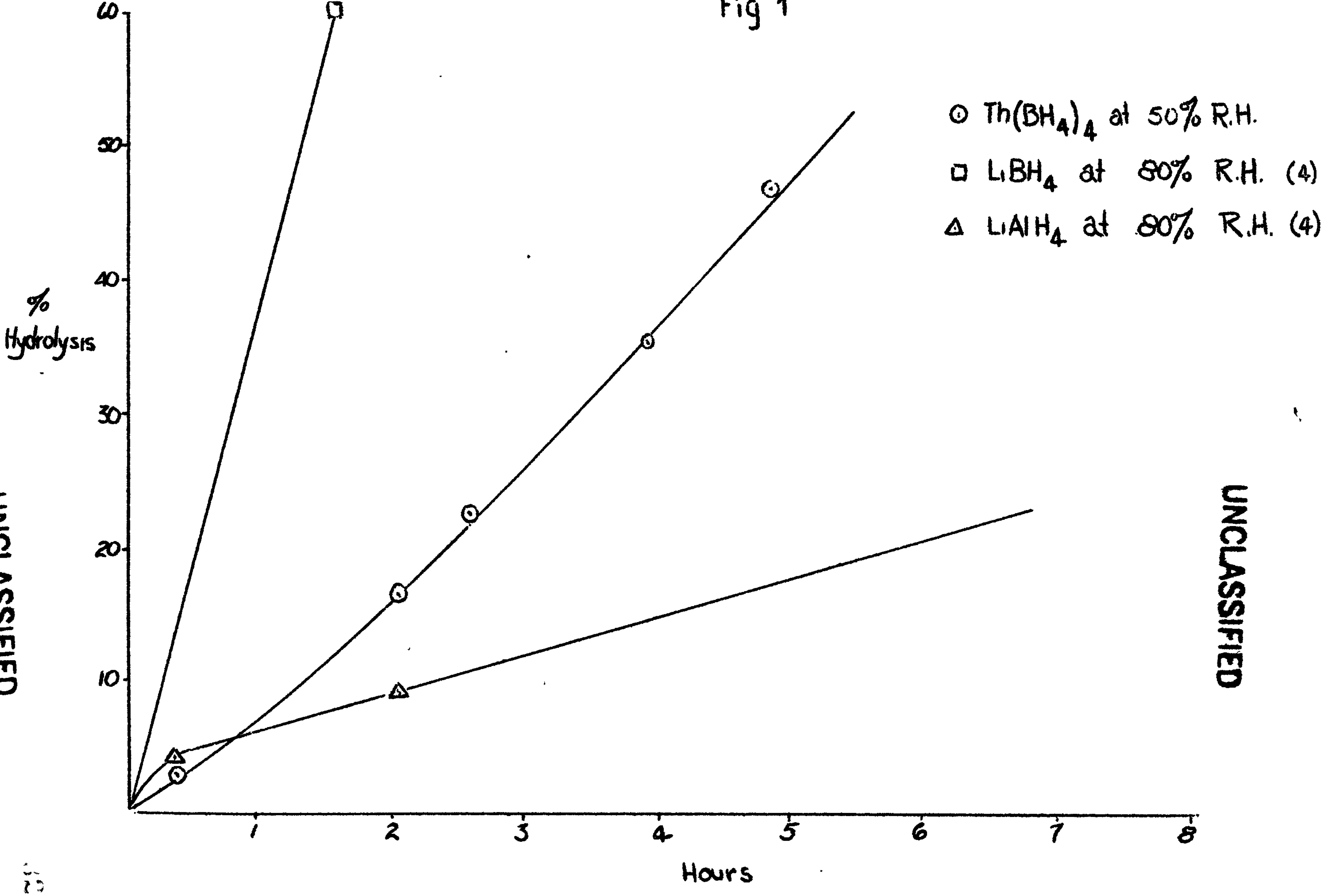
(2) The density of the material has been determined to be 2.59^{5} ± .02 g/cc corresponding to an N_H = 8.62.

(3) Thorium borohydride has been shown to be thermally stable at 150° C for an extended length of time.

(4) The stability of thorium borohydride in air is such that it may be safely handled, although undue exposure will cause loss in purity.

(5) The crystalline compound does not melt below 240° C when decomposition occurs.

Fig 1



(4) H.I. Schlesinger et al, U.S. Navy Reports