[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

The Preparation and Properties of the Group IV-B Metal Borohydrides[1]

BY H. R. HOEKSTRA AND J. J. KATZ

The borohydrides are a relatively new and interesting class of compounds. The first member of this class, aluminum borohydride, was discovered in 1939 with the preparation of a compound containing aluminum, boron and hydrogen in the ratio 1:3:12, *i. e.*, AlB_3H_{12}.[2] More intensive study led to the assignment of the formula $Al(BH_4)_3$.[3] Subsequently, the beryllium,[4] lithium,[5] sodium,[6] potassium[6] and magnesium[7] borohydrides were prepared. The aluminum, beryllium, lithium and magnesium borohydrides were obtained by the action of diborane on the corresponding metal alkyl; the sodium and potassium compounds by the action of diborane on the corresponding tri- and tetramethoxyborohydrides.

The first heavy metal borohydride to be prepared was uranium borohydride.[8] Since no uranium alkyl compound was known, the reaction between anhydrous uranium tetrafluoride and aluminum borohydride was successfully employed

$$UF_4 + 2Al(BH_4)_3 \longrightarrow U(BH_4)_4 + 2AlF_2BH_4 \quad (1)$$

One of the most interesting properties of the metal borohydrides is their volatility. Aluminum and beryllium borohydrides have (extrapolated) boiling points of 44.5 and 91.3°, respectively, which made these the most volatile known compounds of these two elements. Similarly, uranium(IV) borohydride is by far the most volatile known compound of tetravalent uranium. We have, therefore, undertaken a study of the borohydrides of some other metals and we are able to report here the preparation and some of the properties of zirconium, hafnium and thorium borohydrides. As anticipated, these borohydrides are indeed the most volatile known compounds of these elements. In addition, we have studied titanium(III) borohydride, and plan in the near future to report the results of studies directed to the preparation of neptunium and plutonium borohydrides.

Experimental

Apparatus.—The vacuum apparatus and technical methods used for this work have been described by Stock,[9] Burg[10] and by Schlesinger and Walker,[11] and need not be discussed in detail here.

Materials.—Aluminum, lithium and sodium borohydrides used in our experiments were obtained through the courtesy of Professor H. I. Schlesinger. Since aluminum borohydride decomposes slowly on storage at room temperature, it was purified by fractionation before each experiment, and its purity checked by vapor pressure measurement (119 mm. at 0°).

Thorium Tetrafluoride.—Anhydrous thorium fluoride was a very pure sample obtained through the courtesy of Dr. F. S. Spedding.

Hafnium Oxide.—Obtained from the Chemical Commerce Co. of Newark, N. J. It was a special grade rated as 99.5% hafnium oxide; spectrographic analysis in this Laboratory showed only 0.2% zirconium to be present.

Zirconium hydride and titanium hydride were obtained from the Metal Hydrides Co., Beverly, Mass.

Titanium tetrachloride, C. p. grade, was purified by two distillations in vacuum, and condensation at −80°, which served effectively to separate it from hydrolysis products and hydrogen chloride.

Experimental Results

Thorium Borohydride.—This compound was prepared by a reaction similar to that employed for the preparation of uranium(IV) borohydride by Schlesinger and Brown, *i. e.*, the action of aluminum borohydride at room temperature on the anhydrous metal fluoride

$$ThF_4 + 2Al(BH_4)_3 \longrightarrow Th(BH_4)_4 + 2AlF_2BH_4 \quad (2)$$

Because of the relatively low volatility of thorium borohydride at room temperature, it could not readily be obtained from the reaction mixture by simple fractional distillation and condensation as with the uranium compound. Instead, the reaction was carried out in a tube (20 mm. in diameter) fitted with a standard taper joint and an inner-seal collar half-way up the side of the vessel.

A sample of anhydrous thorium fluoride (2.1352 g., 6.93 millimoles) was placed in the reaction tube, which was then attached to the vacuum system and evacuated. An excess of aluminum borohydride (373 cc. at S.T.P., 16.65 millimoles) was condensed on the thorium fluoride and the tube allowed to stand at room temperature for several days. At the end of this period the unreacted aluminum borohydride was pumped off and measured (5.35 millimoles), after which the reaction tube was heated (up to the collar level) at 150° for several hours. The elevated temperature served to disproportionate aluminum difluoroborohydride to aluminum borohydride (3.7 millimoles) which was continuously pumped away, and to non-volatile aluminum fluoride; simultaneously a white crystalline solid sublimed and condensed above the heated zone. The sublimate of thorium borohydride was prevented from falling back into the aluminum fluoride residue by the protective collar. Since 11.30 millimoles of aluminum borohydride had been used, the reaction according to equation (2) was 82% complete. X-Ray investigation by Professor W. H. Zachariasen of the product showed it to be isomorphous with uranium boro-

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[1] Presented in part at the Spring, 1948, Meeting of the American Chemical Society.

[2] H. I. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, **61**, 536 (1939).

[3] H. I. Schlesinger, R. T. Sanderson and A. B. Burg, *ibid.*, **62**, 3421 (1940).

[4] A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940).

[5] H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

[6] H. R. Hoekstra, Ph.D. Thesis, University of Chicago, 1947.

[7] H. I. Schlesinger, *et al.*, U. S. Navy Report, 1945, Contract No's N173 s-9058, s-9820.

[8] H. I. Schlesinger and H. C. Brown, to be published.

[9] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[10] A. B. Burg, THIS JOURNAL, **56**, 499 (1934).

[11] H. I. Schlesinger and A. O. Walker, *ibid.*, **57**, 622 (1935).

hydride. The melting point of the compound was found to be 204° (with decomposition).

Determination of Formula of Thorium Borohydride.—The formula of the thorium borohydride was established by hydrolysis and a determination of the Th:B:H ratio. A portion of the white solid (0.1382 g.) was transferred (in a dry box) to a 500-cc. hydrolysis bulb through a sidearm and the bulb was attached to the vacuum system through a stopcock and joint; the sidearm was then sealed off and the bulb evacuated. An excess of water was distilled into the bulb at $-80°$, and the bulb then warmed to room temperature with the stopcock closed. After completion of the rather vigorous reaction, the stopcock was opened to a manometer and the hydrogen and water vapor pressure measured (after equilibrium had been reached). Since thorium borate formed by the reaction was insoluble, its effect on the water vapor pressure was considered to be negligible. The volume of hydrogen liberated (correcting for water vapor pressure) was 169.5 cc. Hydrolysis studies on borohydrides have established the general equation

$$BH_4^- + 2H_2O \longrightarrow BO_2^- + 4H_2 \qquad (3)$$

Consequently, the calculated hydrogen volume for 0.1382 g. of thorium borohydride is 169.9 cc. (at S.T.P.). The solution and precipitated solids were analyzed for thorium (found 105.5 mg., 0.465 millimole) and boron (found, 20.33 mg., 1.879 millimoles). Thus, the calculated empirical formula is $Th_{0.98}B_{3.96}H_{16.00}$, ($Th(BH_4)_4$).

All analytical results for boron and metals in thorium and the other metal borohydrides were obtained through the courtesy of R. Bane, K. Jensen and R. Telford of the Analytical Section of this Laboratory. Boron was determined by distillation as methyl borate and titration of the liberated boric acid; the metals were estimated gravimetrically as oxides.

Hafnium Borohydride.—The first attempts to prepare hafnium borohydride were by the action of aluminum borohydride on hafnium tetrafluoride, analogous to the preparation of thorium and uranium borohydrides. Hafnium oxide was first converted to the anhydrous tetrafluoride by anhydrous hydrogen fluoride at 500° in an all-nickel apparatus. The temperature of hydrofluorination was found to be critical in that increasing temperature resulted in excessive volatilization of the hafnium fluoride, while lower temperatures resulted in exceedingly slow fluorination which proceeded no further than the oxyfluoride stage. Analysis of the product obtained at 500° showed it to be 98.5% HfF_4. Surprisingly enough, treatment of this fluoride with aluminum borohydride either at room temperature for several days, or on heating in a sealed vessel at 65° for six hours gave no indication of any reaction.

The preparation of hafnium borohydride was successfully accomplished by using the double salt $NaHfF_5$ instead of HfF_4. The double salt is readily obtained by fusing hafnium tetrafluoride with an equimolecular quantity of sodium fluoride. Treatment of this compound (0.7468 g., 2.52 millimoles) with an excess (211.6 cc. at S.T.P., 9.45 millimoles) of aluminum borohydride resulted in reaction. After allowing the reactants to stand for several days at room temperature, the volatile components were pumped off and fractionated; 6.96 millimoles of aluminum borohydride were recovered. For complete reaction, assuming an equation analogous to the uranium and thorium cases

$$NaHfF_5 + 2Al(BH_4)_3 \longrightarrow Hf(BH_4)_4 + 2AlF_2BH_4 + NaF \qquad (4)$$

5.04 millimoles would have been used, indicating that the reaction was only 50% complete. Heating the nonvolatile residue resulted in the recovery of an additional 0.78 millimole of aluminum borohydride which probably originated from disproportionation of aluminum difluoroborohydride.

A white solid melting at 29° with a vapor pressure of about 15 mm. at 25° was separated from the aluminum borohydride by fractionation. This compound forms beautiful transparent crystals and may be easily sublimed in vacuum at room temperature.

The formula of this substance was established in the same manner as the thorium compound except that the hafnium compound was distilled into the hydrolysis bulb. The empirical formula obtained on hydrolysis and complete analysis was $Hf_{1.03}B_{3.98}H_{16.00}(Hf(BH_4)_4)$.

Zirconium Borohydride.—The methods used here were entirely analogous to those used for the preparation of the hafnium compound, with but one exception. The zirconium dioxide available for our experiments was even less reactive toward hydrogen fluoride than the hafnium oxide, thus making it impossible to prepare the fluoride without excessive volatilization of the product. Zirconium fluoride was therefore prepared from zirconium hydride which was found to react completely (98.7%) within one and one-half hours at 400–450°. In this case, also, ZrF_4 proved to be completely unreactive; the double salt, $NaZrF_5$, however, reacted readily with aluminum borohydride.

Zirconium borohydride can also be prepared by the action of aluminum borohydride on anhydrous zirconium chloride, prepared by the method of Smith and Harris.[12] This method of borohydride preparation as compared to the reaction of aluminum borohydride on the double fluoride has the advantage of being essentially complete in a short time; its disadvantage lies in the formation of a complex mixture of aluminum chloroborohydrides which are similar to those encountered in the preparation of titanium borohydride from titanium tetrachloride (see below) and which are difficult to separate. Several careful fractionation steps are required to obtain zirconium borohydride free of aluminum and chlorine by this reaction.

Analysis of a product obtained by the $ZrCl_4$-$Al(BH_4)_3$ method gave the formula $Zr_{1.04}B_{4.06}H_{16.00}$.

Titanium(III) Borohydride.—The reaction of titanium tetrachloride with aluminum borohydride is complex; immediate reduction to the III oxidation state occurs with the simultaneous formation of aluminum and titanium(III) chloroborohydrides (see below). Titanium(III) borohydride has, therefore, been prepared only by the action of lithium borohydride on titanium tetrachloride. Titanium tri- and tetrafluorides do not react with aluminum borohydride, nor does the double salt $NaTiF_4$. Whether the double salts $NaTiF_5$ or Na_2TiF_5 will react remains to be determined.

The apparatus used to prepare titanium(III) borohydride is shown in Fig. 1. A sample of purified titanium tetrachloride was placed in tube A, and an excess of lithium borohydride on the sintered glass disk D. The lithium compound was covered with a glass wool plug G to prevent dusting of the extremely light powder. With the system evacuated, the titanium tetrachloride was allowed to distil through the lithium borohydride. The less volatile reaction product, a green solid, was trapped in U_a with a $-45°$ bath, while a more volatile fraction, trapped in U_b with liquid nitrogen, was identified as diborane. The tube U_a was removed from the system by sealing off the constrictions at C_1 and C_2. Analysis was carried out in the manner described above. A typical analysis obtained on the green solid gave the following results (in millimoles): hydrogen, 9.87, boron, 2.43, titanium, 0.823 and chlorine, <0.006. The calculated empirical formula is therefore $Ti_{1.00}B_{2.96}H_{12.00}(Ti(BH_4)_3)$, and the equation for this reaction is

$$2TiCl_4 + 8LiBH_4 \longrightarrow 2Ti(BH_4)_3 + 8LiCl + B_2H_6 + H_2 \qquad (5)$$

The reaction of titanium tetrachloride with aluminum borohydride was investigated in some detail, but since the reaction is complex and the titanium compound obtained is a mixed chloroborohydride, this work will be reviewed only briefly. The reaction between $TiCl_4$ and $Al(BH_4)_3$ is violent unless carried out at a low temperature (-30 to $-40°$) and results in the formation of

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[12] E. F. Smith and H. B. Harris, THIS JOURNAL, **17**, 654 (1895).

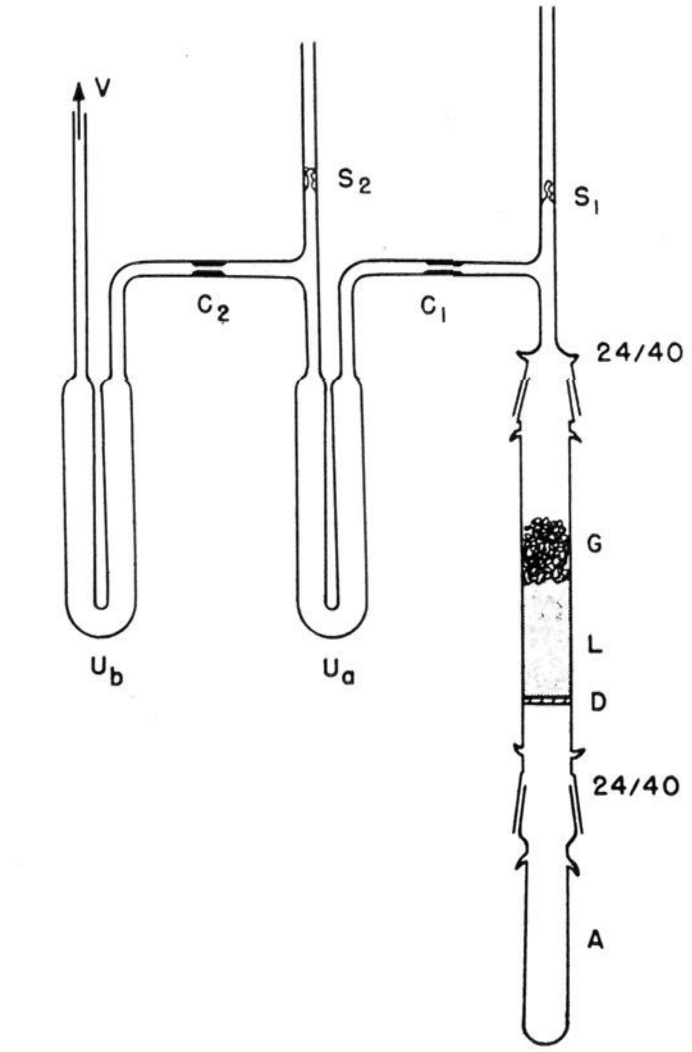

Fig. 1.—Apparatus for the preparation of titanium(III) borohydride: A, reaction tube; C, seal-off constriction; D, sintered glass disk; G, glass wool; L, lithium borohydride; S, magnetic breaker seal.

mono- and dichloroborohydrides of aluminum (hereafter designated as A and B) as well as titanium(III) monochloroborohydride (C). A is a colorless liquid at room temperature which disproportionates rapidly to aluminum borohydride and B. The latter compound is a white solid at 25° which shows no appreciable tendency toward further disproportionation. C is a deep blue solid having a vapor tension slightly higher than B (about 1 mm. at 25°). The simplified equation for the reaction may be expressed

$$2TiCl_4 + 3Al(BH_4)_3 \longrightarrow 2\underset{(C)}{TiCl(BH_4)_2} + 3\underset{(B)}{AlCl_2BH_4} + B_2H_6 + H_2 \quad (6)$$

B and C are nearly equal in volatility, making their separation very difficult. Analysis of a partially fractionated product gave these results

Element	H	B	Cl	Al	Ti
Millimoles	39.28	9.72	6.38	0.81	4.64

Subtraction of the calculated amounts of chlorine, boron and hydrogen combined with the aluminum in compound B left the following

Element	H	B	Cl	Ti
Millimoles	36.04	8.91	4.76	4.64

The empirical formula $Ti_{1.03}Cl_{1.06}B_{1.98}H_{8.00}$ (or $TiCl(BH_4)_2$) is thus obtained for compound C. Confirmation of this formula was obtained by passing C over lithium borohydride, which resulted in the conversion of the blue solid to the green titanium(III) borohydride.

Vapor Pressure and Thermal Stability of Group IVB Borohydrides.—Since volatility is one of the most interesting properties of the borohydrides, an effort has been made to obtain reasonably accurate vapor pressure values over as large a temperature range as feasible. Measurements on thorium borohydride were carried out using the method described by Burg and Schlesinger.[13] Thorium borohydride has no measurable vapor pressure at room temperature, thus requiring a slight modification in the apparatus. A side-arm which *could be sealed off was placed* on the tensimeter bulb to permit addition of the solid borohydride. At 150° solid thorium borohydride appears to be quite stable, since very little decomposition may be noted. On passing thorium borohydride vapors through a tube heated to 300°, however, complete decomposition occurs with the formation of a bright, metallic mirror. Analysis of the mirror gave the empirical formula $Th_{1.00}B_{3.83}$; X-ray investigation showed the material to be amorphous.

Vapor pressure measurements on zirconium and hafnium borohydrides were made in the simplified apparatus shown in Fig. 2. A carefully purified sample of the borohydride was distilled into a tube A which was equipped with a short manometer M. The tube was then sealed off at C, and submerged (to the level L) in a constant temperature

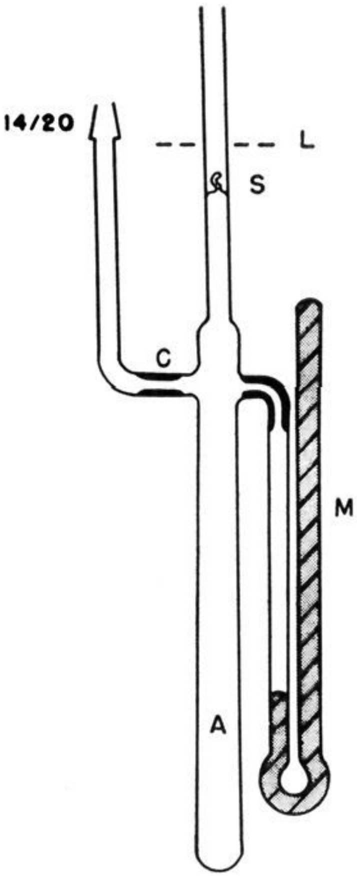

Fig. 2.—Apparatus for determination of borohydride vapor pressure: A, vapor pressure tube; C, seal-off constriction; M, manometer; S, magnetic breaker seal.

TABLE I

VAPOR PRESSURES OF THORIUM, HAFNIUM AND ZIRCONIUM BOROHYDRIDES (MM.)

Compound ⟶ Temp., °C.	Thorium borohydride	Hafnium borohydride	Zirconium borohydride
0		2.2	1.8
10		4.7	4.2
25		14.9	15.0
30		21.0	20.3
40		36.0	33.2
50		56.4	52.2
130	0.05		
150	.20		

TABLE II

COMPARISON OF PHYSICAL PROPERTIES OF THORIUM, HAFNIUM AND ZIRCONIUM BOROHYDRIDES

Compound ⟶ Property	Thorium borohydride	Hafnium borohydride		Zirconium borohydride	
Melting point in °C.	203	29.0		28.7	
Boiling point (extrapolated)	..	118		123	
Heat of sublimation, kcal./mole	(21)	13.0		13.6	
Heat of vaporization, kcal./mole	..	9.6		9.3	
Heat of fusion, kcal./mole	..	3.4		4.3	
$\log p = -\frac{A}{T} + B$		Solid	Liquid	Solid	Liquid
A		2844	2097	2983	2039
B		10.719	8.247	10.919	8.032

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(13) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 785 (1937).

bath controlled to within ±0.05°. Pressure measurements were made with a Gaertner cathetometer; the readings were reproducible within ±0.05 mm. Values given are averages of three separate readings. Corrections were made for variation in mercury density with temperature. Exposure of the borohydrides to elevated temperatures was held to a minimum by keeping the tube A at −80° while the bath temperature was being changed. After completion of the measurements, no measurable pressure of non-condensable gas could be detected. The borohydride was then removed from the closed system by sealing the tube to the vacuum line and breaking the magnetic seal S.

The observed vapor pressures are given in Table I, and a log *p* *vs.* $1/T$ plot from which (extrapolated) boiling points, heats of sublimation and vaporization were obtained is shown in Fig. 3. Table II compares the physical properties of the three borohydrides.

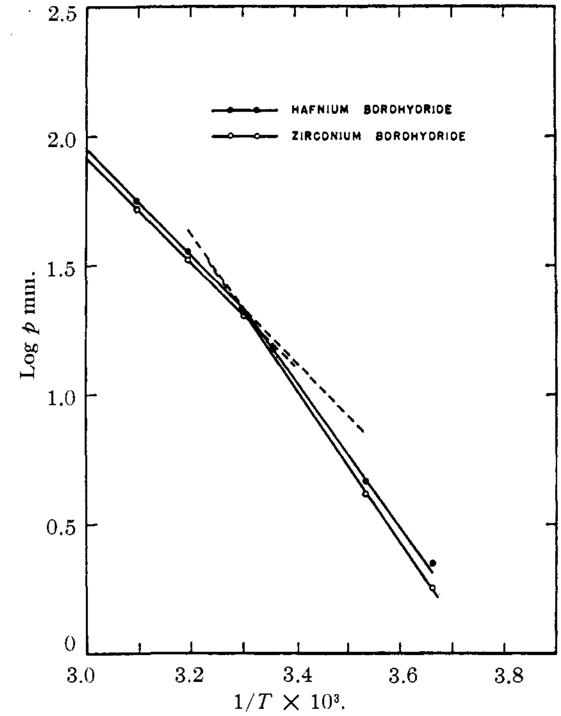

Fig. 3.—Vapor pressures of hafnium and zirconium borohydrides.

The more salt-like, non-volatile, borohydrides (sodium, thorium) are stable indefinitely at room temperature, while the more covalent, volatile borohydrides (aluminum, uranium, zirconium, hafnium) decompose very slowly to form hydrogen and non-volatile compounds of indefinite composition. This decomposition has been shown to take place principally in the vapor phase.[8] Titanium(III) borohydride is an exception, decomposing completely within several days at room temperature to hydrogen and a non-volatile solid which deposits on the walls of the container as a metallic mirror. The other volatile borohydrides have been shown to decompose in a similar fashion at elevated temperatures, but the titanium compound is the only one to undergo this reaction at room temperature. As a result, no attempts have been made to study the vapor tension of $Ti(BH_4)_3$. The formulas of the metallic borides have not been definitely established since, in the case of titanium borohydride it would be difficult to distinguish between TiB_3 and a mixture of metallic boron with a titanium boride containing less boron, *e. g.*, TiB_2. A study of the decomposition of titanium borohydride at 25° (Fig. 4) indicates that the reaction is autocatalytic. Fractionation of the volatile products indicated that the principal product was hydrogen. Only 13–14% of the borohydride decomposed to form diborane.

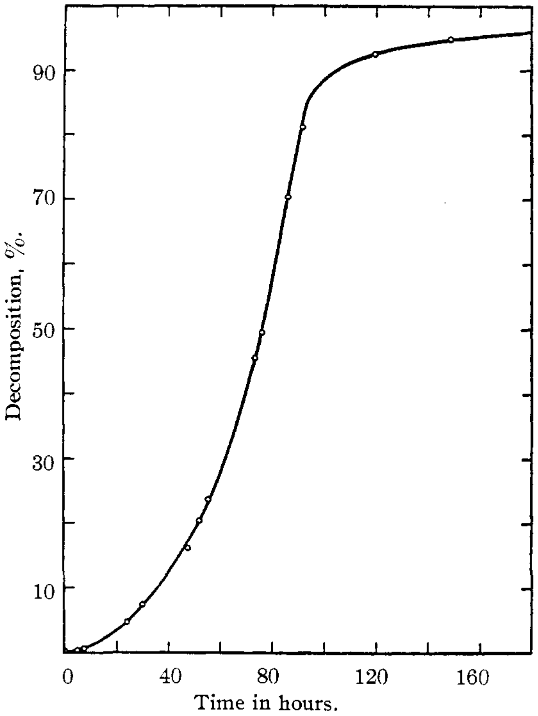

Fig. 4.—Decomposition of titanium(III) borohydride at 25°.

Solubility of Thorium Borohydride in Various Solvents.—Thorium borohydride was placed (dry box) in a small Pyrex tube fitted with a standard taper joint. The tube was attached to the vacuum line and about 1 ml. of diethyl ether (dried over sodium hydride) condensed on the borohydride. The tube was then removed from the vacuum system after having been filled with dry nitrogen, capped securely, and placed in a constant temperature bath at 20° (±0.05°) for forty-eight hours. Two samples were then quickly pipetted from the clear supernatant solution. Sample A (after weighing) was treated directly with dilute hydrochloric acid and analyzed for thorium content. In order to investigate the possibility of etherate formation at 0° sample B was weighed into a tube similar to that described above, placed on the vacuum system, and the ether removed as completely as possible at ice-bath temperature. The non-volatile residue was weighed and analyzed for thorium:

Sample	Weight, g.	Wt. after pumping at 0°C., g.	Thorium, g.	Calcd. soly. in g./100 g. ether
A	0.2939	....	0.0750	47.0
B	.2890	0.1408	.0731	46.5

Experiment B shows that 2.1 millimoles of ether per millimole of borohydride were found, indicating an etherate of probable composition $Th(BH_4)_4 \cdot 2(C_2H_5)_2O$ forms. Further investigation of the etherate disclosed that a portion of the thorium borohydride can be recovered from the coördination compound on heating, but not without partial decomposition.

The solubility of thorium borohydride in tetrahydrofuran was determined to be 23.6 g./100 g. solvent. Thorium borohydride appears to be insoluble in benzene.

Discussion

The remarkably high volatility shown by the borohydrides of beryllium, aluminum, and uranium has been shown to extend to the elements of group IV-B of the Periodic Table as well; these compounds in every case are more volatile than any other known compound of that oxidation state of the metal.

The reducing power of the borohydrides, *e. g.*, their stability in dry air and toward water is apparently dependent to a large extent on the metal ion associated with the borohydride grouping. Metals with electronegativities of one or less in the Pauling scale[14] form borohydrides which show considerable salt-like character (low volatility, high melting point). Using the Schlesinger terminology,[5] these compounds may be said to show greater BH_4^- character, while borohydrides of more electronegative metals show more $BH_3 + H^-$ character. Thus borohydrides of aluminum, beryllium, zirconium, and hafnium inflame violently when exposed to dry air. Further evidence that the reducing power of the borohydrides may be interpreted as due to hydride character is shown in the reaction of various borohydrides with titanium tetrachloride. Aluminum, beryllium, and even lithium borohydride will reduce titanium to the (III) state, whereas sodium borohydride does not reduce titanium (IV) at room temperature.

The success enjoyed in the preparation of thorium borohydride from the tetrafluoride at first seemed to indicate that the reaction of the metal fluoride with aluminum borohydride was a general method applicable to at least all Group IV-B metals. The inactivity of the tetrafluorides of hafnium, zirconium, and titanium showed this assumption to be incorrect, and it appears that a minimum metal/fluorine ion ratio exists beyond which the metal fluoride is unreactive toward aluminum borohydride; this minimum occurs between thorium and hafnium. Fusion of the metal fluoride with sodium fluoride to form the double salt appears to render the compound more reactive in some manner, and this observation may prove an effective tool in the preparation of other borohydrides.

Acknowledgment.—We wish to thank Professors H. I. Schlesinger and H. C. Brown for their interest in this work, and for making some of the intermediate compounds available to us. Thanks are due to Professor W. H. Zachariasen for the X-ray determinations.

Summary

1. Borohydrides of all the members of Group IV-B of the Periodic Table have been prepared. Tetravalent borohydrides of thorium, hafnium and zirconium, and the trivalent compound of titanium were obtained.

2. The borohydrides of thorium, zirconium and hafnium were found to be the most volatile known compounds of these elements. Titanium (III) borohydride is the most volatile known compound of trivalent titanium.

3. Thorium borohydride is the most salt-like compound in this group, resembling the lithium and sodium compounds in its properties. Hafnium and zirconium borohydrides are low melting, volatile solids more nearly resembling aluminum borohydride. Titanium(III) borohydride is the least stable compound of this type prepared to date.

4. As yet, no general method for the preparation of Group IV-B metal borohydrides has been discovered. The reaction of aluminum borohydride with the anhydrous metal tetrafluoride can be used for thorium. Fusion of the tetrafluoride with sodium fluoride to form the corresponding double salt is necessary in the case of hafnium and zirconium, while the titanium salt has been prepared by the action of lithium borohydride on titanium tetrachloride.

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(14) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 64.