degassed. After the reaction was over, the black product which had settled out of the solution was collected on the sintered glass disc by rotating the apparatus. The water was distilled back into the original flask (leaving crystalline sodium metaborate behind in the second flask) and was used to wash the precipitated product. The filtration, distillation and washing were repeated five times to remove all soluble impurities. The reaction vessel was then connected to a vacuum system and the water was distilled away. Hydrogen was admitted to the vessel and the flask containing the product was quickly removed and capped.

A 0.2712-g. sample of the product was dissolved in dilute hydrochloric acid and analyzed for cobalt[7] and boron; found: 0.2404 g. Co; 0.0222 g. B. These two elements account for 96.8% of the sample weight; the Co:B ratio is 1.99 to 1.

An 0.1862-g. sample of the pyrophoric material was exposed to air and the oxidation was completed at 300°. The product weighed 0.2110 g. as compared with a value of 0.2096 g., calculated for conversion of Co_2B to a mixture of CoO and CoB.

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[7] G. Spacu and J. Dick, *Z. anal. Chem.*, **71**, 97 (1927).

CHICAGO, ILL.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Uranium(IV) Borohydride[1]

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Uranium(IV) borohydride was prepared by the reaction of uranium(IV) fluoride with excess aluminum borohydride, $UF_4 + 2Al(BH_4)_3 \rightarrow U(BH_4)_4 + 2AlF_2(BH_4)$. Its green crystals are volatile at room temperature. Its relatively low molecular weight and the volatility give it special interest. Reactions with water, methanol and hydrogen chloride were observed. At room temperature the borohydride, when sealed in evacuated glass containers, may be kept for long periods of time with only very slight decomposition; the rate of decomposition remains small up to about 70° in the absence of catalysts. At 100° it decomposes at a moderate rate to give uranium(III) borohydride, a reddish-brown solid, as shown by the equation: $U(BH_4)_4 \xrightarrow{100°} U(BH_4)_3 + {}^1/_2H_2 + {}^1/_2B_2H_6$. At 150–200° uranium(IV) borohydride undergoes decomposition to give a mirror of silvery metallic appearance. The reaction is: $U(BH_4)_4 \rightarrow UB_4$ (or $U + 4B$) $+ 8H_2$. Uranium(IV) borohydride is fairly stable to dry air; uranium(III) borohydride is pyrophoric.

Treatment of uranium(IV) fluoride with aluminum borohydride at room temperature results in the formation of lustrous, dark green, moderately volatile crystals which, in larger aggregates, appear almost black. These have been shown by analysis, vapor density measurements and chemical behavior to consist of uranium(IV) borohydride, $U(BH_4)_4$. The stoichiometry of the reaction leads to the equation

$$UF_4 + 2Al(BH_4)_3 \longrightarrow U(BH_4)_4 + 2Al(BH_4)F_2$$

but the non-volatile water reactive residue has not been isolated or identified by analysis.

The compound volatilizes without melting. Of the uranium(IV) derivatives known at the time of its discovery it is by far the most volatile,[2] as shown by the sublimation pressures recorded in Table II.

In view of the special objectives of this study, major emphasis was placed on the stability of the new compound at various temperatures and in the presence of possible catalysts. This phase of the study was necessarily largely empirical. The results obtained are, therefore, only briefly described, as are a number of observations made about the chemical behavior of the compound.

At temperatures below 70° uranium(IV) borohydride is fairly stable. Even at 70°, samples kept for from 5–10 days showed only 1 to 4% decomposition. Other samples kept for several years at room temperature have undergone only very slight change, noticeable chiefly at the surfaces of the crystals. The decomposition seems to occur primarily in the gas phase and to be catalyzed by finely divided metals.

At 100° the decomposition is considerably more rapid and leads to the formation of a reddish-brown, non-volatile solid. The amounts of hydrogen and diborane formed in the reaction suggest the equation

$$2U(BH_4)_4 \xrightarrow{100°} 2U(BH_4)_3 + B_2H_6 + H_2$$

The composition of the solid is further confirmed by its color[3] and by the fact that it generates 12 moles of hydrogen by hydrolysis per mole of the uranium(IV) borohydride decomposed in its formation. The fact that the brown decomposition product is non-volatile, pyrophoric and likely to detonate on contact with air, made it difficult to isolate and handle and prevented its further study in the time available.

At higher temperatures (>150°) uranium(IV) borohydrides undergoes rapid decomposition to yield a mirror of silvery appearance and hydrogen contaminated with only traces of volatile boron compounds. The amount of hydrogen obtained indicates the reaction equation[4]

$$U(BH_4)_4 \longrightarrow UB_4 \text{ (or } U + 4B) + 8H_2$$

In contrast to the brown decomposition product, described above, $U(BH_4)_4$ does not react rapidly with air at room temperature. Its reactions with water, methanol and hydrogen chloride are represented by the equations

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[1] New Developments in the Chemistry of Diborane and the Borohydrides. X. The nomenclature employed herein is explained in paper I of this series, THIS JOURNAL, **75**, 186 (1953).

[2] The monomethyl derivative, prepared subsequently, is somewhat more volatile. H. I. Schlesinger, H. C. Brown, L. Horvitz, A. C. Bond, L. D. Tuck and A. O. Walker, *ibid.*, **75**, 222 (1953).

[3] Uranium(III) derivatives are described as being reddish-brown. E. M. Peligot, *Ann. chim. phys.*, [3] **5**, 20 (1842); A. Rosenheim and H. Lobel, *Z. anorg. Chem.*, **57**, 234 (1908).

[4] Although a uranium boride of the composition UB_4 has been described [L. Andrieux, *Ann. chim.*, [10] **12**, 423 (1929)] we did not obtain evidence on which to base a decision about the identity of the material of the mirror.

$$U(BH_4)_4 + 16H_2O \longrightarrow U(OH)_4 + 4H_3BO_3 + 16H_2$$

$$U(BH_4)_4 + 16CH_3OH \longrightarrow U(OCH_3)_4 + 4B(OCH_3)_3 + 16H_2$$

$$U(BH_4)_4 + 4HCl \longrightarrow UCl_4 + 2B_2H_6 + 4H_2$$

Several attempts were made to prepare uranium(IV) borohydride by metathesis in solvents. Some evidence of reaction was observed. For example, treatment of uranium(IV) fluoride with lithium borohydride in the presence of ether led to the formation of a green, ether-soluble product. Evaporation of the ether from the solution gave a last fraction which was considerably less volatile than ether, which had a definite green color, and which co-distilled with the residual ether. A complete separation could not be effected. We may have been dealing with an etherate unstable at room temperature. Since the reaction of aluminum borohydride with uranium(IV) fluoride worked so satisfactorily, we abandoned attempts to develop a synthesis based directly on the alkali metal borohydrides.

Experimental Part

Materials. (a) **Aluminum Borohydride.**—Originally aluminum borohydride prepared by the interaction of trimethylaluminum and diborane was used.[5] In the preparation of larger quantities, difficulty was encountered in obtaining a sample of the aluminum compound sufficiently pure to produce uranium borohydride of satisfactory quality. The use of aluminum borohydride prepared from aluminum chloride and an alkali metal borohydride[6] overcame the difficulty.

(b) **Uranium(IV) fluoride** was prepared by the method of Grosse.[7]

Preparation of Uranium(IV) Borohydride.—Uranium(IV) fluoride (27.6 g. or 0.0876 mole) was introduced through arm A into the reaction vessel, R (Fig. 1), which was then connected to the vacuum system through ground joint D. Arm A was sealed at C. The last traces of moisture were removed from the fluoride by heating R to 350° with continuous pumping until the pressure fell to 10^{-4} mm. Aluminum borohydride (11.2 g. or 0.157 mole) was distilled into the cooled reaction vessel through a −40° trap which prevented contamination of the final product with mercury. (Mercury appeared to hasten the decomposition of the uranium borohydride.) The reaction vessel was then sealed off at B and allowed to warm to the temperature of an ice-salt-bath, in which it remained for 8–12 hours. To assure completion of the reaction, the mixture was maintained at room temperature for another 3 hours.

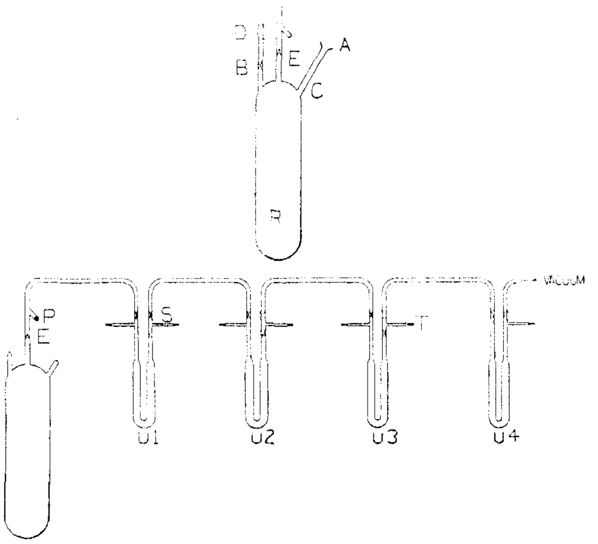

Fig. 1.—Apparatus for the preparation of uranium borohydride.

After R had been reattached to the vacuum line through the magnetic breaker tube, E, it was again cooled to −196°. The four U-tubes were evacuated; U-4 was cooled to −196°, and U-3 to −10 to −15°. The seal on E was broken and R was allowed to warm to room temperature. Uranium(IV) borohydride collected in U-3, unchanged aluminum borohydride in U-4. By consecutively cooling U-2 and U-1 with ice–salt-baths, one-third of the total uranium compound was collected in each of the first three U-tubes. Sometimes it proved desirable to warm R to 50–60° to hasten the sublimation which was usually completed in about 8 hours.

After collection of the uranium(IV) borohydride, the first three U-tubes were sealed off. For this purpose they were immersed in liquid nitrogen and pumped for at least 30 minutes to prevent formation of a mirror at the seal. The unchanged aluminum borohydride was transferred from U-4 to the vacuum line through a vacuum tube opener.

There was obtained 17.0 g. of uranium borohydride (0.057 mole). Of the 0.157 mole of aluminum borohydride, 0.019 mole was recovered. The yield, based on aluminum borohydride consumed, was 83%.

Aluminum Borohydride–Uranium(IV) Fluoride Ratio.—In a number of preparations a careful check was maintained on the ratio of aluminum borohydride consumed in the reaction (the borohydride was present in excess), to uranium(IV) fluoride originally present. The results, summarized in Table I, are consistent with the equation $UF_4 + 2Al(BH_4)_3 \rightarrow U(BH_4)_4 + 2AlF_2(BH_4)$.

TABLE I

REACTION BETWEEN URANIUM(IV) FLUORIDE AND ALUMINUM BOROHYDRIDE

Reactants		Products		
Uranium fluoride, mmoles	Aluminum borohydride, mmoles	Uranium borohydride, % yield	Aluminum borohydride (recovered), mmoles	$\frac{Al(BH_4)_3 \text{ consumed}}{UF_4 \text{ (initial)}}$
1.02	2.50	..	0.52	1.94
27.2	71.5	90.2	15.2	2.07
8.05	23.1	87.2	6.93	2.01
6.76	22.6	81.1	8.61	2.07

· **Hydrolysis and Analysis.**—A tube, into which a sample of uranium(IV) borohydride had previously been sublimed, was attached through the tube opener to the vacuum line. A small quantity of water was distilled into the tube and allowed to stand for 3 hours, during which time evolution of hydrogen was completed. After the removal and measurement of the hydrogen, the residue was treated with sulfuric acid and methanol. The methyl borate thus formed was collected and titrated in the usual way. The remaining solution was evaporated, the residue treated with nitric acid and then ignited to convert uranium to the oxide, U_3O_8. The latter process was carried out in microchemical apparatus with appropriate microchemical procedures. There were obtained 19.3 ml. of hydrogen and 0.0150 g. of U_3O_8, and 5.68 ml. of 0.0378 *N* barium hydroxide were required to titrate the methyl borate. These data correspond to the atomic ratios U:B:H = 0.0536:0.215:0.862, or to the empirical formula $U_{1.00}B_{4.01}H_{16.1}$.

Vapor Pressures. Molecular Weight.—Vapor pressures were measured in our early work using mercury manometers in contact with the vapor. It was observed that the surface of the manometer became coated with the reddish-brown powder later identified as uranium(III) borohydride and it appeared that the mercury vapor and the mercury surface were catalyzing the decomposition. We therefore adopted the use of an all-glass Bourdon gage to determine the sub-

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

[6] H. I. Schlesinger, H. C. Brown and E. K. Hyde, *ibid.*, **75**, 209 (1953).

[7] A. V. Grosse, "A New Crystalline Hydrate of Uranium Tetrafluoride and Its Dehydration to Anhydrous Uranium Tetrafluoride," S. A. M. Laboratory Report, Columbia University, N. Y.

limation pressures.[8] In this way the borohydride vapor came into contact only with glass. Representative data are summarized in Table II.

TABLE II

SUBLIMATION PRESSURE DATA FOR URANIUM(IV) BOROHYDRIDE

The calculated values were obtained by the equation: $\log P_{\text{mm}} = -4{,}265/T + 13.354$

Temp., °C.	34.2	40.2	48.2	54.3	61.3
P, mm. (obsd.)	0.30	0.56	1.23	2.15	4.00
P, mm. (calcd.)	0.30	0.55	1.20	2.12	3.98

The molecular weight was determined by vaporizing a measured weight of the solid in a known volume at a known temperature and observing the pressures exerted. Here also the pressures were determined by balancing the pressure of the vapor in a glass Bourdon gage against an air pressure measured with a mercury manometer. Contact of the vapor with all substances other than glass was avoided and decomposition of the vapor during the measurement was decreased to a minimum. Representative data are summarized in Table III.

TABLE III

DATA FOR DETERMINATION OF MOLECULAR WEIGHT

Wt. of uranium borohydride, g.	0.0461
Volume, ml.	283.3
Temp., °C.	79.0
Obsd. press., mm.	14.35
Residual press., mm.	0.49
Press. of vapor, mm.	13.86
Calcd. mol. wt.	305.7

Several such determinations yielded values in the range 305–310 with an average of 308. In view of the experimental difficulties and the necessity of operating only slightly below the saturation pressure of the borohydride, the agreement with the theoretical value (291) may be considered satisfactory. It confirms the monomeric formula for the borohydride.

Stability.—In a typical experiment 0.341 g. of the borohydride was placed in a sealed glass tube, maintained at 70° for 10 days. The tube was then opened and 0.326 g. was recovered. A total of 15 mg. was lost, indicating 4% decomposition into other products.

It was noted that the amount of borohydride decomposed was not proportional to the initial quantity used, suggesting that the decomposition must occur chiefly in the vapor phase. This conclusion was supported by the observation that, in a vessel so large that all the borohydride was vaporized, decomposition was much more extensive than in smaller vessels. The decomposition appeared to occur on the glass surface and was increased by an increase of the surface in contact with the borohydride vapor. The rate of decomposition is also markedly increased by contact of the vapor with finely divided metals.

Solubility.—A few experiments of the effect of solvents on uranium(IV) borohydride were made in connection with the study of certain of its reactions. Solvents with ionizable hydrogen, such as water, alcohols, etc., react with the compound. Ethyl ether appeared to form a 1:1 etherate, stable at −80°. Approximately 2 g. of the borohydride dissolved in 100 ml. of the solvent, but the borohydride could not be completely recovered from the solution. The last portion of ether appears to co-distil with the borohydride.

The borohydride dissolved only slightly in *n*-heptane. When the latter was distilled from the solution, a small amount of the borohydride was carried along and condensed with the distillate. This dilute solution was clear and colorless at room temperature, but became distinct green at −80°. The borohydride recovered from the heptane solution was of good quality and did not appear to be affected chemically by the solvent.

The borohydride did not react with highly purified benzene. The solubility was also small in this case. Distillation of benzene from a −20° trap effectively separated the solvent from the borohydride.

Decomposition of Uranium(IV) Borohydride at Elevated Temperatures.—A weighed amount of uranium(IV) borohydride was volatilized and passed through two U-tubes. The first was maintained in different experiments at approximately 150, 165, 170 or 200°; the second U-tube was maintained at 390–400° to decompose material which escaped decomposition in the first tube. The rate of distillation was maintained at 160–180 mg. per hour.

In a typical experiment 0.2615 g. of the borohydride was distilled in a period of 1.6 hours through the two tubes in series maintained at 196–197° and 390–393°, respectively. In the first tube a silvery mirror which weighed 0.1965 g. was deposited. In the second tube (390°) the deposit was 0.0475 g. The product in the first tube gave a ratio of boron-to-uranium of 3.75:1. The material dissolved easily in dilute hydrochloric or nitric acid with the evolution of hydrogen gas. The characteristic boron hydride odor could be detected in the evolved gas. These characteristics agree well with the properties ascribed to UB_4 by Andrieux.[6]

Acknowledgment.—The assistance of A. C. Bond, J. J. Katz, R. C. Lad and L. D. Tuck with individual preparations and experiments is gratefully acknowledged.

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[8] See, for example, A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Part I, Interscience Publishers, Inc., New York, N. Y., 1949, p. 166.