

(b.p. 67.5–68° at 750 mm.). The over-all yield was 89%. The last column shows that even in the most favorable experiment 14.5% of the methyl borate was lost as part of the acid layer.

A mixture of 570 ml. (500 g.) of the azeotrope and 570 ml. of ligroin (b.p. 110°, previously washed with sulfuric acid) was treated with two portions of 20 ml. of sulfuric acid. Only 4.8% of the ester was lost and 98.1% of the methanol was removed. Distillation of the solvent led to 91.2% yield of ester boiling from 67.5–68.5°.

Azeotropic Separation.—A mixture of 2800 g. of the azeotrope and 1400 g. of carbon disulfide was fractionally distilled with the aid of the column employed for the preparation of the azeotrope. The carbon disulfide–methanol azeotrope distilled at 38°. The distillate separated into two layers, of which the lower one (97% carbon disulfide–3% methanol) was returned to the still. At the end of 45 hours of operation, methanol removal was complete, as indicated by the rise in boiling point to that of carbon disulfide, 46°. The products were a carbon disulfide–methanol fraction of 2105 g., a fraction from 46 to 67.5° of 88 g. (73% ester) and 1940 g. of pure methyl borate, b.p. 67.5–68.5°. The yield was 92.3%. The reaction time could probably be greatly decreased by the use of a more efficient column.⁶

Lithium Chloride Separation.—The effectiveness of a number of salts in separating the methanol from the azeotrope was studied. Data are summarized in Table IV.

The addition of 120 g. of anhydrous lithium chloride to 1000 g. of the azeotrope caused the mixture to separate into two layers.⁷ The lower one consisted of a solution of lithium

(6) The advantage of recycling a portion of the carbon disulfide is lost if the carbon disulfide–methanol mixture contains as little as 1.5% of methyl borate, for then separation into two layers does not occur. This difficulty is avoided by use of a good fractionating column.

(7) Although a smaller amount (80 g.) of the salt seems to saturate the solution, the larger quantity gives somewhat better results.

TABLE IV

EXTRACTION OF METHANOL FROM THE AZEOTROPE WITH SALTS

Salt used	LiCl	NaCl	CaCl ₂	Ca-(NO ₃) ₂	AlCl ₃	MgCl ₂	Zn-Cl ₂
G. salt per 135 g. azeotrope	13	30	14	30	8.0	15	46
Purity of methyl borate, %	99.6	98.0	92.5	90	85	98.2	99.6

chloride in methanol plus some suspended salt and contained from 3.6 to 4.0% of the methyl borate present in the azeotrope. The upper layer contained about 96% of the methyl borate of from 99.5 to 99.7% purity; the slight contamination was methanol.

The methanol was recovered from the lower layer by distillation. Below 90°, the small quantity of the methyl borate present distilled as the azeotrope. At a pot temperature of from 95 to 115°, 96% of the methanol was recovered practically pure. At this stage the lithium chloride was obtained partly as a powder and partly as readily powdered lumps.

By raising the temperature to 160°, the remaining 4% of the methanol could be recovered. When that was done, the lithium chloride was obtained as a hard cake which, though usable, was inconvenient to handle. It is, therefore, recommended that heating the residue above 115° be avoided if the lithium chloride is to be re-used in subsequent separations.

Acknowledgment.—The assistance of Anthony M. Schwartz and E. K. Hyde with individual experiments and preparations described in this paper, is gratefully acknowledged.

CHICAGO, ILL.

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

Sodium Borohydride, Its Hydrolysis and its Use as a Reducing Agent and in the Generation of Hydrogen¹

BY H. I. SCHLESINGER, HERBERT C. BROWN, A. E. FINHOLT, JAMES R. GILBREATH, HENRY R. HOEKSTRA AND EARL K. HYDE

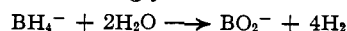
RECEIVED MARCH 15, 1952

Sodium borohydride reacts slowly with water ultimately to liberate 4 moles of hydrogen per mole of the compound at room temperature, or 2.4 l. per gram. The reaction is greatly accelerated by rise of temperature or by the addition of acidic substances, for which latter purpose boric oxide is convenient and effective when the objective is the generation of hydrogen. Particularly striking is the catalytic effect of certain metal salts, especially that of cobalt(II) chloride. Thus pellets of sodium borohydride containing only 5% of the cobalt salt react as rapidly as those containing 10 times that amount of boric oxide. The effect of the cobalt salt is ascribed to the catalytic action of a material of empirical composition, Co₂B, which is formed in the initial stages of the reaction.

The hydrolysis of sodium borohydride is of interest in connection with the use of the compound as a reducing agent in aqueous solutions² and because of its potential usefulness for the generation of hydrogen whenever or wherever the use of the compressed gas is inconvenient. Under appropriate conditions, 2.37 l. of hydrogen (gas at S.T.P.) are liberated per mole of the compound, as compared with 1.1 l. for calcium hydride and 2.8 l. for lithium hydride. At ordinary temperatures, however, only a very small percentage of the theoretical amount of hydrogen is liberated at an

appreciable rate, since the initial moderately rapid rate soon decreases after the borohydride and the water have been mixed. As a result, not only may the aqueous solution of the compound be effectively used as a chemical reagent, but a large part of the salt may actually be recovered unchanged from such solutions by removal of water *in vacuo*.³

It is evident that the decrease in the initial rate of hydrogen evolution is due to the increasing pH of the solution⁴ which in turn is caused by the formation of the strongly basic metaborate ion



Thus the initial generation of hydrogen may be

(1) New Developments in the Chemistry of Diborane and of the Borohydrides. IX. For an explanation of the nomenclature employed, see paper I, *THIS JOURNAL*, **75**, 186 (1953).

(2) (a) H. I. Schlesinger, H. C. Brown and A. E. Finholt, *ibid.*, **75**, 205 (1953). (b) S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 122 (1949); unpublished work of G. W. Schaeffer and A. Stewart. (c) A. Stewart, Master's Thesis, University of Chicago (1948).

(3) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, *THIS JOURNAL*, **75**, 199 (1953).

(4) See also M. Kilpatrick and C. D. McKinney, Jr., *ibid.*, **72**, 5474 (1950).

largely prevented by dissolving the borohydride in a slightly basic solution rather than in pure water; on the other hand, the complete hydrolysis of the borohydride may be achieved rapidly by the addition of acid to the aqueous solution.

These facts are of considerable importance in the use of sodium borohydride as a reducing agent in aqueous solution. Thus, in some such reactions, *e.g.*, the reduction of ferric ion for analytical purposes, it is desirable to carry the reaction out in slightly alkaline solution and with an excess of the borohydride. After reduction is complete the latter may be decomposed rapidly by adding an acid and raising the temperature.

When, on the other hand, the borohydride is to be used as a means of generating hydrogen, rapid reaction is desired. Since for both laboratory as well as for the field generation of hydrogen, the source of the latter is most conveniently used in the form of pellets, the acidic accelerator should be one readily and safely mixed and compressed with the solid borohydride. Several such substances are described in the following. Another means, also to be discussed more fully, is the incorporation in the pellet of certain salts which act as catalysts, and which, in amounts much smaller than required of the acid accelerators, are as effective as the latter independently of *pH* of the solution.

Discussion of Accelerators

Acidic Accelerators.—Pellets containing equal weights of sodium borohydride and one of 30 different solid acidic materials were compared with respect to their rate of hydrolysis under standard conditions. The acids varied greatly in effectiveness but, in general, the stronger acids produced the greater acceleration. Examples of effective accelerators are oxalic acid, succinic acid, phosphorus(V) oxide and aluminum chloride. Boric oxide, although derived from a weak acid, was very effective, presumably because of its reaction with sodium metaborate to give the tetraborate. The latter was actually precipitated and could be recovered from the reaction mixtures involving sodium borohydride-boric oxide pellets. Typical data are shown in Table I.

A study of the rate of hydrolysis in several different buffer solutions of the same *pH* indicated that the rate is dependent only on the *pH* and is independent of the specific acids and salts used in the buffer. For example, within the limits of experimental error, the rates of hydrogen evolution were identical in solutions buffered at *pH* 7.0 by the McIlvaine buffer (citric acid and disodium acid phosphate), the Clark and Lubs buffer (potassium diacid phosphate and sodium hydroxide) and the Sörenson buffer (disodium acid phosphate and monopotassium diacid phosphate).

Experiments in which the *pH* of the solutions was maintained by Clark and Lubs buffers demonstrated clearly the marked dependence of the rate of hydrolysis on the hydrogen ion concentration. Thus at *pH* 7.0 the reaction was 90% complete in 5 minutes; at *pH* 7.4 it was only 67% complete in the same time.

Although no detailed quantitative study was

made of the effect of water temperature and the effect of borohydride to water ratio, it was observed that the higher the initial water temperature and the smaller the ratio of water to borohydride, the more rapid the hydrolysis. With oxalic acid pellets and small quantities of water the reaction was so violent that the pellet was heated to incandescence.

Certain of the acid accelerators presented problems in mixing and pelleting. Mixtures of sodium borohydride with oxalic acid or with aluminum chloride sometimes caught fire as they were being ground in the preparation of the pellets. Phosphorus(V) oxide could not readily be incorporated into a firm pellet which would not disintegrate.

All of the pellets containing acids were reasonably stable to heat and to air of ordinary moisture content. Pellets containing boric oxide were particularly stable to heat and appeared to offer a number of advantages for ready generation of hydrogen.

Catalytic Accelerators.—A number of substances well known for their general catalytic effectiveness, such as colloidal platinum, platinized asbestos, a platinum oxidation catalyst, copper-chromic oxide, activated charcoal and Raney nickel were investigated to test the feasibility of this type of accelerator. All of these had a decided influence. Search for a more practical type of material led to a study of manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) chlorides. These salts all reacted rapidly with borohydride solutions and gave dark suspensions or precipitates which were probably borides. These precipitates had a marked catalytic action which was highest in the case of the cobalt product, somewhat less for nickel and least for iron, manganese and copper.

Pellets containing 5% of anhydrous cobalt(II) chloride⁵ liberated hydrogen at a satisfactory rate and were approximately as effective as pellets containing 50% by weight of boric oxide. Typical studies are illustrated in Table II and Fig. 1.

The black material, obtained when cobalt(II) chloride was added to sodium borohydride solutions, rather than cobalt(II) chloride itself, appeared to be the effective catalyst because (1) all of the cobalt salt was transformed into the black material long before the catalyzed generation of hydrogen was complete and (2) the black material, removed from the reaction mixture, washed and dried, retained most of its catalytic effectiveness and brought about hydrogen evolution from a fresh batch of sodium borohydride.

A sample of the black product was prepared and isolated under oxygen-free conditions. Analysis indicated a cobalt to boron ratio of 1.99 to 1. The active catalyst is therefore considered to be a cobalt boride,⁶ Co_2B . The dry product is pyro-

(5) Hydrated cobalt chloride must not be used. When it is ground together with the borohydride, the mixture becomes very hot and turns black, a reaction which might be hazardous with larger quantities. Other anhydrous cobalt salts behave like the chloride, but the latter is the most easily dehydrated and is the most effective per unit weight.

(6) A boride of this composition has been previously described by A. Stock and E. Kuss, *Ber.*, **47**, 810 (1914). It is conceivable that the material is a mixture of metallic cobalt and a cobalt boride, CoB , obtained in constant proportions by weight by the reactions mentioned.

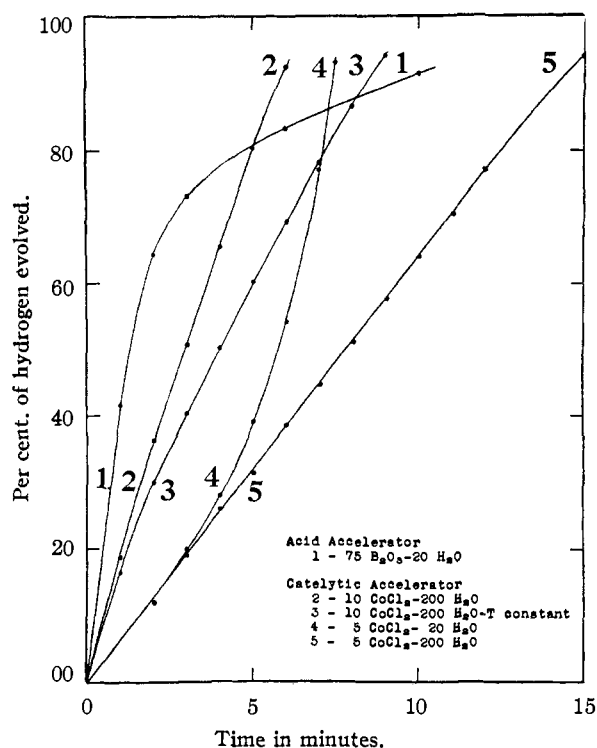


Fig. 1.—Evolution of hydrogen from sodium borohydride solutions.

phoric. The oxidized product appears to be a mixture of cobalt(II) oxide and another cobalt boride which contains only one cobalt atom per atom of boron.

The advantages of pellets containing boric oxide as an accelerator are that they cause no or only a little foaming when added to water and that the solution is not caustic at the conclusion of the reaction. The disadvantages are (1) that, because of decreasing acidity of the solution, the reaction which at its initiation is very rapid, slows down considerably before all of the hydrogen has been generated (Fig. 1, curve 1); (2) that the relatively large amount of boric oxide decreases the yield of hydrogen per gram of pellet; and (3) that certain types of hydrogen generators, used in the past, need modification because of the precipitation of sodium tetraborate.

The advantages of pellets containing the cobalt salt are (1) that, because of the small amount of accelerator required, its use does not significantly reduce the hydrogen yield per gram of pellet; (2) that the black precipitate described is so finely divided and so small in amount as to be negligible; and (3) that the reaction proceeds at an almost constant rate until it is complete (Fig. 1, curves 3 and 5). In fact, if the temperature is allowed to rise, as occurs if only small amounts of water are used, the reaction may be somewhat faster at the end than at the start. The chief disadvantage of the catalysis by cobalt, or other similar salts, is that the solutions become more and more alkaline as the reaction proceeds. As a result more care is required in emptying the generators; the more important effect, however, is that there is considerable foaming. The latter difficulty could probably be over-

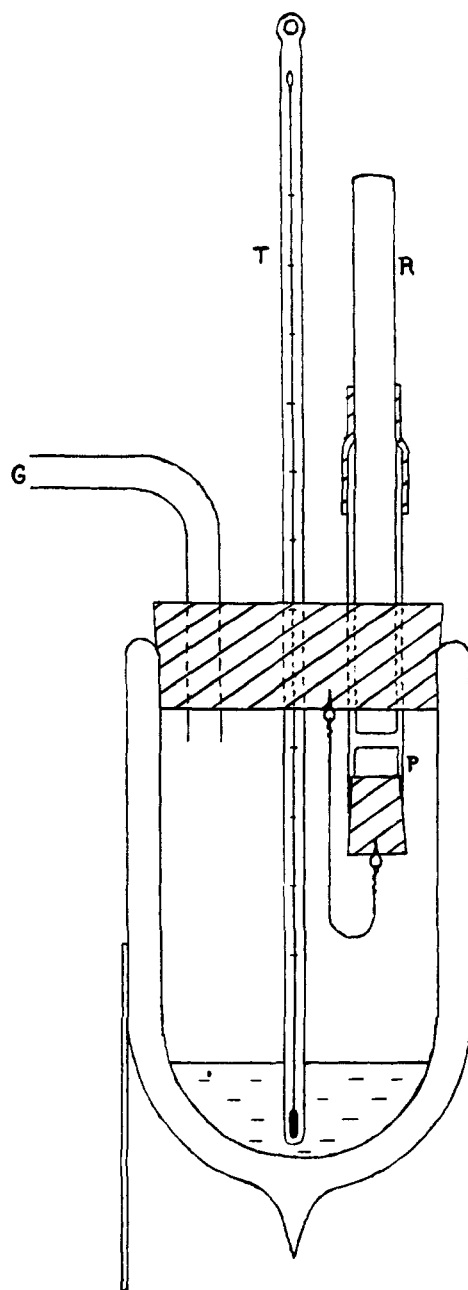


Fig. 2.—Apparatus for hydrolysis of sodium borohydride.

come by use of antifoaming agents or by appropriate design of the generators.

Although further work is required on the more practical aspects of the problem, these studies indicate that pellets of sodium borohydride, containing either 50% of boric oxide or 3-7% of cobalt (II) chloride, furnish a convenient, practical source of hydrogen for field generation or for laboratory use when compressed hydrogen cannot be employed conveniently or economically.

Experimental Part

Rate of Hydrolysis.—The rate of hydrolysis of mixtures of sodium borohydride and accelerators was determined by dropping a pellet of the mixture into water and collecting the hydrogen generated. The pellet was formed in a dry-box with a small pellet press and was weighed in a covered weighing bottle on an analytical balance. The hydrolysis was carried out in a wide-mouth pint dewar flask, equipped

TABLE I
 EFFECT OF ACID ACCELERATORS ON RATE OF HYDROGEN EVOLUTION

Accelerator	Amount, g./100 g. NaBH ₄	Hydrogen liberated, %		Accelerator	Amount, g./100 g. NaBH ₄	Hydrogen liberated, %		
		10 min.	15 min.			3 min.	6 min.	10 min.
Calcium chloride	100	0		Oxalic acid	60	90	93	95
Sodium borofluoride	100	15		Succinic acid	60	86	92	95
Phthalic acid	75	54		Malonic acid	60	88	93	94
Salicylic acid	100	54		Citric acid	60	75	81	85
Alum	100	64		Tartaric acid	60	72	78	83
Benzoic acid	100	64		Oxalic acid	75	Violent reaction		
Phthalic anhydride	75	65		Succinic acid	75	95.5	98	99
Sulfamic acid	60	69		Malic acid	75	98	93	95
Ammonium alum	100	74		Citric acid	75	84	88	90
Ammonium chloride	100	75		Boric oxide	75	74	84	89
Maleic anhydride	100	76		Oxalic acid	100	Violent reaction		
Sodium acid sulfate	100	78		Succinic acid	100	Very fast		
Sodium diacid phosphate	100	80		Citric acid	100	96	99	..
Aluminum sulfate	100	82		Tartaric acid	100	95	98	..
Maleic acid	100	85		Mucic acid	100	89	93	95
Ammonium carbonate	100	90		Boric oxide	100	86	95	97.5

with a 3-hole rubber stopper which held a thermometer, a gas outlet tube, and a length of 12-mm. tubing sufficiently large to hold a pellet (Fig. 2). A glass rod was inserted in the 12-mm. tubing and a rubber sleeve, lubricated with glycerol, made a gas-tight seal.

In performing a hydrolysis, a weighed pellet was placed in the 12-mm. tubing, and a cork was placed in the bottom end to retain the pellet. The rubber stopper with its attachment was placed in the dewar flask, in which the desired quantity of water had been placed. The gas evolved was collected in a graduated cylinder over water. The reaction was initiated by pushing the glass rod, R, against the pellet and the cork. The pellet then fell into the water, while the cork was held to the tubing by a wire connection. The gas was collected and corrected to standard conditions.

Experiments at constant temperature were run in a similar manner. In these experiments the dewar vessel was replaced by a 30-mm. test-tube or small flask which was immersed in a constant temperature bath. When small quantities of water were involved, the temperature was maintained by immersing the test-tube intermittently in a cold bath with vigorous agitation of the contents of the tube.

Acidic Accelerators.—The result obtained with a number of representative acidic materials are summarized in Table I. All experiments were begun at 25° with 20 g. of water per gram of sodium borohydride. For those accelerators which gave 95% or better hydrogen in 10 minutes, the temperature rose to 47–55°.

Catalytic Accelerators.—Results obtained in comparable experiments utilizing 0.15 g. of the metal chloride with 20 g. of water (at 25°) per g. of sodium borohydride are summarized in Table II. It is apparent that maximum effectiveness was reached with the cobalt salt.

TABLE II

EFFECT OF CATALYTIC ACCELERATORS ON RATE OF HYDROGEN EVOLUTION

Accelerator, chlorides	Hydrogen liberated, %		
	5 min.	10 min.	15 min.
Manganese(II)*	Slower than CuCl ₂		
Iron(II)	38	53	65
Cobalt(II)	46	97	..
Nickel(II)	42	74	99
Copper(II)	32	43	49

* Manganese(II) chloride was not included in this particular set of experiments. However, in other comparable experiments under slightly different conditions, in 10 min. the amount of hydrogen liberated was 30% versus 43% for copper(II) chloride.

The effect of temperature upon the rate of hydrogen evolution is shown in Table III. Pellets were prepared containing 10% by weight of anhydrous cobalt(II) chloride and were dropped into water weighing 200 times the weight of

the borohydride. The temperatures were maintained constant during the reaction. The time noted in Tables III and IV is for complete hydrogen evolution.

TABLE III

EFFECT OF TEMPERATURE ON HYDROGEN EVOLUTION

Temp., °C.	1	15	25	40
Time, min.	56	17	9	2.5

Hydrogen could be generated at temperatures below 0° if water-methanol or water-ethylene glycol mixtures were used. A pellet containing 20% by weight of anhydrous cobalt(II) chloride was dropped into 20 times its weight of liquid (40% methanol-60% water) at -16°; the hydrogen was completely evolved in 22 minutes. In a similar experiment with 34% ethylene glycol-66% water, the hydrogen was obtained in 9.5 minutes.

The rate of hydrolysis of the cobalt(II) chloride pellets was affected much less than that of the acid accelerated pellets by the ratio of water to borohydride used. Pellets containing 10% by weight of the cobalt salt were dropped into varying amounts of water; in one set of experiments the temperature was maintained constant at 25°, in the other the water temperature was allowed to rise as a result of the generated heat. The data are summarized in Table IV.

TABLE IV

EFFECT OF WATER-BOROHYDRIDE RATIO ON HYDROGEN EVOLUTION

Wt. H ₂ O Wt. NaBH ₄	Temp. 25° (constant) Time, min.	Temp. 25° (initial) Time, min.	Max. temp., °C.
5	17	1.8	>83
20	9	2.5	58
100	..	4	38
200	9	6	32
400	9	6	30
800	8	9	25

Cobalt Boride.—The preparation of the black catalytic substance was carried out in a vessel shaped somewhat like a dumbbell with a right-angle bend at its center. The two ends of the vessel were 50-ml. flasks. These were connected to the L-shaped portion by standard taper joints. A side-neck from the L-tube carried a stopcock and could be connected to a vacuum pump. The neck of the flask in which the reaction was carried out was equipped with a sintered glass disc and a side-neck with a standard taper joint through which the reagents could be added.

The boride was prepared by adding solid sodium borohydride in an atmosphere of hydrogen to 20 ml. of 0.77 M cobalt(II) chloride solution (0°) which had been previously

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 cobalt⁷ 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 Co₂B to a mixture of CoO and CoB.

(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) Borohydride¹

By H. I. SCHLESINGER AND HERBERT C. BROWN

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Uranium(IV) borohydride was prepared by the reaction of uranium(IV) fluoride with excess aluminum borohydride, $UF_4 + 2Al(BH_4)_3 \rightarrow U(BH_4)_4 + 2AlF_3(BH_4)$. 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:

$$U(BH_4)_4 \xrightarrow{100^\circ} U(BH_4)_3 + \frac{1}{2}H_2 + \frac{1}{2}B_2H_6$$

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



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

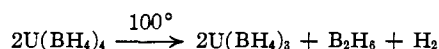
The compound volatilizes without melting. Of the uranium(IV) derivatives known at the time of its discovery it is by far the most volatile,² as shown by the sublimation pressures recorded in Table II.

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

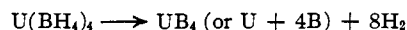
occur primarily in the gas phase and to be catalyzed by finely divided metals.

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



The composition of the solid is further confirmed by its color³ 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 equation⁴



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

(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.*, **87**, 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.