is almost no competition but as f increases, the experimental curves I and II rise until the theoretical value for competition is exceeded and one fatty acid anion displaces more than one dye anion.

The crude solubility data can be used to approximate a lower limit of binding at any value of added fatty acid. If the concentration of free acid is assumed to be equal to the solubility of elaidic acid, an estimate of the fraction bound when $1 - r/r_0 = 0.025$ can be made; this value is about twice that calculated from $F/n = (1 - r/r_0)$, so that there is indeed very much less competition than would be expected. The almost complete lack of competition must be explained. The complicating presence of micelles in solutions of fatty acids most probably is not responsible for this situation. Micelle formation would of course be expected to decrease the competing ability of the fatty acid, but as more fatty acid is added to the system there should be an even greater tendency toward micelle formation with a resultant further decrease in competition. Experimentally it is observed that as increasing amounts of fatty acid are added competition increases until one fatty acid is effective in displacing more than one dye anion. If, however, there were additional sites of low reactivity available only to fatty acid, not to methyl orange, it would be possible to account for the almost complete lack of competition at low values of f. Recent work of Karush,[19] Karush and Sonenberg,[20] Scatchard, Scheinberg and Armstrong[21,22] and Teresi[18] has shown that the binding of anions by serum albumin can best be described in terms of more than a single set of reactive sites.

The fact that a single fatty acid anion is effective in displacing more than one dye anion requires explanation. Similar results have been obtained in other laboratories[12,13] in studies of the methyl orange–dodecyl sulfate competition system. When Klotz, Triwush and Walker attempted to apply simultaneous equations of the type of Eq. (1) and (2) to methyl orange and dodecyl sulfate, their calculations yielded the result that more dodecyl sulfate was bound than has been added. They attributed this discrepancy to omission of electrostatic interaction terms from the binding equations. Their results for the methyl orange–salicylate system, on the other hand, did not show this inconsistency. Karush[13] treated the methyl orange–dodecyl system in another way and found that in the r range of 3 to 7 seven bound detergent anions are equivalent to eleven bound dye anions; he has explained this in terms of the heterogeneity of the binding sites of serum albumin.

While it is true that the results of these investigations cannot be explained simply in terms of a single set of binding loci of identical reactivity toward a given anion for which the two species compete without interaction they also cannot be explained completely by the theory of the inhomogeneity of the binding sites of serum albumin. At low values of f this theory is quite adequate; at high values of f additional explanation is needed. It seems quite probable that the topography of the albumin molecule is such that the addition of a long chain molecule at one binding site causes steric hindrance at another, thus permitting one fatty acid anion to displace more than one dye anion.

NEW YORK 21, N. Y. RECEIVED JUNE 9, 1950

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(19) F. Karush, THIS JOURNAL, **72**, 2705 (1950).

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(21) G. Scatchard, I. H. Scheinberg and S. H. Armstrong, Jr., *ibid.*, **72**, 535 (1950).

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

The Pyrolysis of Diborane and the Synthesis of Pentaborane[1]

BY L. V. McCARTY AND P. A. DI GIORGIO

It has been shown that pentaborane containing only small amounts of dihydropentaborane can be synthesized from diborane in reasonable yields. Reaction time and temperature can be traded against each other which results in a relatively wide range of operating conditions. Hydrogen definitely helps in the more efficient conversion of diborane to pentaborane.

Introduction

Even since Alfred Stock[2] first demonstrated methods of making tetraborane in small amounts, methods of synthesizing one boron hydride from another have been of great interest to inorganic chemists. Recent work by Professor H. I. Schlesinger[3] and his co-workers at the University of Chicago has made diborane the easiest boron hydride to obtain in quantity. It is in the natural course of events, then, that improved syntheses for other boron hydrides from diborane should be sought.

Much work has already been done on the preparation of pentaborane by thermal decomposition of diborane in circulatory and single pass systems[2–7] particularly since the diborane synthesis of Schlesinger and Burg[4] in 1931. This paper deals with a study of the best conditions for carrying out this reaction. Some additional information pertinent to the synthesis of other boron hydrides can also be found in the data.

Experimental Part

Materials.—The diborane used in these experiments was prepared by the reaction of boron fluoride etherate with

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(1) This work was done on Army Ordnance Contract T U 1-2000.

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

(3) Unpublished work of H. I. Schlesinger and H. C. Brown and collaborators, at present contained in reports to various government agencies and in University of Chicago doctoral theses.

(4) Burg and Schlesinger, THIS JOURNAL, **53**, 4321 (1931).

(5) Burg and Schlesinger, *ibid.*, **55**, 4019 (1933).

(6) Stock and Mathing, *Ber.*, **69**, 1456 (1936).

(7) Schlesinger and Burg, *Chem. Rev.*, **31**, 13 (1942).

lithium hydride.[2] The diborane storage cylinder was maintained at −18° except for relatively short periods when it was allowed to come to room temperature for transfer of diborane to other vessels. Little deterioration occurred during the four to five month periods each cylinder was used. Analysis by distillation for a typical tank gave the following compositions in mole per cent.: 99.4% diborane and 0.6% non-condensable gas at the beginning; and 97.2% diborane, 1.5% tetraborane and 1.3% non-condensable gas at the end.

Electrolytic hydrogen was purified before use by passage through a copper-packed tube at 500° followed by drying with anhydrous calcium chloride, then Drierite, and finally, in the single pass work, by passage through a trap packed with metal helices and cooled in liquid nitrogen.

The nitrogen used for flushing the system contained less than 0.4% oxygen and was dried by passage through Drierite and, in the single pass work, a trap packed with metal helices and cooled with liquid nitrogen.

Analyses.—Analysis of the products was by distillation in an Automatic Low Temperature Fractional Distillation Apparatus, Hyd Robot Model, Serial No. H576, manufactured by the Podbielniak Super Contactor Company. The gaseous sample volume was usually between 200 and 1450 cc. The approximate error to be expected in this range is 15 cc. of gas for the total sample, and this figure will usually represent a loss, seldom a gain. All analyses were made at 100 mm. pressure.

Another error that comes into the analysis is the slight volatility of hexaborane at 15°. In the technique used some hexaborane, if present, will come over as a part of either the pentaborane or dihydropentaborane fraction, usually the latter. Hexaborane does not seem to be formed in appreciable amounts except at the higher temperatures.

Still another difficulty and source of error is the instability of dihydropentaborane during the analysis. It seems to polymerize to a brown, gummy substance, and at the same time evolves a gas boiling at a lower temperature. So long as the distillation is performed reasonably rapidly at 100 mm. pressure, the error does not seem too serious.

Conversion in the tables is defined as the per cent. of diborane changed to some other substance. The mole per cent. yields of various products are calculated on the boron content of the diborane which is "converted."

Circulating Gas System Runs

Apparatus.—The apparatus was a simplified form of that described by Stock and Mathing.[5] Substantially it consisted of an 11.5-liter elongated bulb, a sylphon bellows pumping station, a glass reactor, a products trap and a manometer sealed between the trap and storage bulb which completed the cyclic system. The reactor and trap were made with ground glass joints to facilitate removal from the system. These, and the vacuum line which entered the system near the manometer, were greased with Apiezon L.

Operation.—In order to speed the work it was necessary to keep certain variables at reasonably fixed values while other effects were studied. Except where otherwise specified then, the system was charged with 102–106 mm. of diborane at room temperature which corresponds to 1.82–1.88 g. of reactants.

The pumping speed was maintained within the limits 1.84–1.93 liters/min., and the reactor volume that was heated is 153 cc. Since the temperature of the reactor also influences the time the gas spends in the reactor, the residence time varies between 2.7 and 3.3 seconds per pass except where otherwise specified.

In overnight runs, which varied between 16 and 22 hours duration, the pump was first started and then the heat turned on. In one hour runs the reaction temperature was first attained and then the pump turned on, since otherwise the time required to get up to temperature would have been an appreciable fraction of the run.

The temperature of the gas depended very much upon the part of the 10″ × 1$^1/_4$″ reactor it was in. Only the middle half was within 5° of the indicated temperature, and the first and last quarters were considerably lower.

A Dry Ice-bath in trichloroethylene was used on the products trap to remove mainly pentaborane and dihydropentaborane from the gas phase.

When other gases were mixed with diborane they were added to it slowly over one complete pumping cycle, and then mixed further by at least two hours recycling before the reaction was started.

Results

The results of this study divide themselves into certain parts which are considered separately, though, for the sake of economy of space, Tables I and III contain the data from the investigation of temperature, hydrogen concentration and nitrogen concentration which was assumed to be an inert gas. Table II is devoted to data obtained from an investigation of the efficiency of product traps described in the text, and Table IV is concerned with the time the gases spend in the reaction zone at various temperatures which is called residence time.

Temperature.—Tables I and III are subdivided into groups depending upon the ratio of moles of hydrogen or nitrogen to diborane, and each of the sudivisions is arranged in order of increasing temperature. In every case the conversion (diborane reacting) increases with increasing temperature, which is neither unexpected nor unusual, but the change in the proportions of products is of great importance. The yield of solids increases with increasing temperature, while the yield of the unstable dihydropentaborane decreases. The yield of pentaborane increases with increasing temperature in all but one case, and in this instance (Table I—runs No. 6 through 11) the yield goes through a maximum. The apparent discrepancy between the 250° results of Tables I and III will be considered in the discussion of trapping efficiency.

Hydrogen Concentration.—In Tables I and III the hydrogen concentration increases progressively by subdivision, except for the last subdivision of Table I in which nitrogen was substituted for hydrogen. Comparing equal temperatures the conversion of diborane decreases with increasing hydrogen concentration, and there is also a general decrease in the yield of solids with two minor exceptions in the tables which are within the experimental error. The effect of hydrogen on the relative proportions of pentaborane and dihydropentaborane is complex. At 200°, in Table I, increasing hydrogen concentration seems to favor dihydropentaborane, but at 225° under the same conditions pentaborane alone is favored apparently to the exclusion of dihydropentaborane.

With better product trapping and shorter run times (Table III) both pentaborane and dihydropentaborane are favored by small increases in hydrogen concentration, while larger increases favor the pentaborane alone.

Nitrogen as an Inert Diluent.—In Table I the effects of nitrogen as an added gas can be compared with pure diborane and the effect of added hydrogen. There seems to be a decrease in the diborane converted paralleling the hydrogen case, but it is not as large an effect. Further, two other effects of hydrogen, lowered solids yield and increased pentaborane yield, are absent.

Trapping Efficiency.—Several times while obtaining the data of Table I a fog was observed escaping from the products trap while immersed in Dry Ice. This was attributed to condensation of the products in the gas phase with entrainment in the moving gas stream. It was believed that such material when recycled through the reactor would react further to give solids which were not always wanted. In order to obviate this effect, a series of packed traps were made to compare with trap 1 which allowed substantially unobstructed flow of gas through it. Trap 2 required the gas to pass through at least 1″ of $^1/_8$″ stainless steel helices, while trap 3 put the gas through 3$^3/_4$″ of $^1/_8$″ stainless steel helices, and trap 4 included a 5″ section packed with Pyrex glass wool. The data of Table II show that the amount of conversion is not greatly affected by the type of trap, but that the character of the products did change. The decrease in the yield of both pentaborane and solids while dihydropentaborane increases may indicate that the latter is an intermediate in the formation of the former.

The use of more efficient trapping at once opened up the possibility of using higher temperatures and shorter run times which was the objective of the work of Table III. The data of Table III were obtained with a glass wool packed trap while an unpacked trap was used in Table I, and this difference in traps is responsible for the large discrepancy between the 250° results of the two tables.

Residence Time.—In Table IV when the product of residence time and number of passes is a constant, an increased time spent in the reaction zone per cycle does not materially affect the amount of conversion within the residence time limits indicated. Run 25 has an appreciably greater conversion than 7, but the product of residence time and number of passes is also greater for 25 than for 7. A more important effect is to be found in the nature of the products formed. Pentaborane and solids are favored by increased residence time at the expense of dihydropentaborane, except when no dihydropentaborane is present. Then the solids yield increases at the expense of pentaborane.

Catalysts.—Possible gaseous catalysts as hydrogen chloride, hydrogen bromide, carbon monoxide and boron trichloride did not produce any significant change in the distribution of the products. It is true that small amounts of products such as chlorodiborane and borine carbonyl were isolated. Boron trifluoride catalyzed a very unusual reaction, for among the products silane was observed in small amount. Apparently the silicon oxide of the glass was reduced, but there was no other gross effect upon product distribution.

TABLE I

MOLE PER CENT. YIELD (BASED ON BORON CONTENT)

Run	Initial H_2/B_2H_6	Temp., °C.	No. of passes	Conv., %	B_4H_{10}	B_5H_9	B_5H_{11}	Solids and residues
Effect of hydrogen on conversion and products: (overnight runs—trap 1 used)								
1[a]	0	175	150	70.9	4	3	85	8
2[a]	0	200	147	92.4	4	43	39	14
3[a]	0	225	145	95.6	3	63	3	31
4	1.0	200	217	88.6	3	40	50	7
5	1.0	225	179	93.0	0	81	0	19
6	5.0	175	168	23.3	4	0	88	8
7	5.0	200	157	57.3	5	28	62	5
8	5.0	225	154	79	1	78	10[b]	11
9[a]	5.0	225	177	83.3	4	82	0	14
10[c]	4.9	225	169	82.1	0	86	0	14
11	4.9	250	180	98.7	0	37	0	63
Effect of nitrogen on conversion and products[d]: (overnight runs—trap 1 used)								
12[a]	0	175	144	52.9	12	0	77	11
13[a]	0	201–216	147	88.3	3	33	47	17
14[a]	0	225–227	145	94.3	5	58	7	30

[a] Analytical technique at fault in these runs with the result that B_4H_{10} figures are too high. [b] Identification as B_5H_{11} doubtful. May have been mainly B_5H_9. [c] Reactor not cleaned between this run and no. 9. [d] Initial nitrogen to diborane ratio = 5.0.

TABLE II

MOLE PER CENT. YIELD (BASED ON BORON CONTENT)

Run	Initial H_2/B_2H_6	Temp., °C.	No. of passes	% Conv.,	B_4H_{10}	B_5H_9	B_5H_{11}	Solids and residues	Remarks
Effects of trapping on reaction products (1 hr. runs)									
15	1.0	228	9.6	66.1	1	64	6	29	1 hr. from time heat turned on till liq. N_2 put on trap. Trap 1 used
16	1.0	229	9.6	69.0	3	61	13	23	Trap 2 used
17	1.0	227	9.6	68.3	3	59	24	14	Trap 3 used
18	1.0	228	9.4	72.1	2	55	32	11	Trap 4 used

TABLE III

MOLE PER CENT. YIELD (BASED ON BORON CONTENT)

Run	Initial H_2/B_2H_6	Temp., °C.	No. of passes	Conv., %	B_4H_{10}	B_5H_9	B_5H_{11}	Solids and residues
Effect of hydrogen with efficient trapping: (one hour runs—trap 4 used)								
19	0	225	9.3	78.4	2	52	30	16
20	0	250	9.4	93.1	<0.5	62	11	27
18	1.0	228	9.4	72.1	2	55	32	11
21	1.0	250	9.3	86.7	0	65	14	21
22	5.1	226	9.4	32.7	12	63	13	12
23	5.0	250	9.5	65.4	1	73	12	14

TABLE IV

MOLE PER CENT. YIELD (BASED ON BORON CONTENT)

Run	Initial H_2/B_2H_6	Temp., °C.	Residence time, sec.	No. of passes	Conv., %	B_4H_{10}	B_5H_9	B_5H_{11}	Solids and residues
Effect of contact time									
1[a]	0	175	3.3	150	70.9	4	3	85	8
24[c]	0	175	20.8	24.1	66.6	4	18	67	11
7[a]	5.0	200	3.2	157	57.3	5	28	62	5
25[a]	4.9	200	6.8	105	70.7	6	56	33	5
10[d]	4.9	225	3.0	169	82.1	0	86	0	14
26[a]	4.9	225	13.0	36.4	87.4	0	78	0	22
18[b]	1.0	228	3.0	9.4	72.1	2	55	32	11
27[b]	1.0	222	6.7	4.1	69.5	2	62	17	19

[a] Trap 1 used. [b] Trap 4 used. [c] 3.74 g. of B_2H_6 used at 210 min. [d] Reactor not cleaned between this run and 9.

Single Pass Runs

Apparatus.—The system used for the single-pass thermal conversion of diborane and diborane–hydrogen mixtures is shown in Fig. 1.

The capillary flowmeters, 2, were filled with either mercury or mineral oil for obtaining a sufficiently wide range of flows without changing capillaries. The diborane flowmeter was calibrated by passing diborane through it at a fixed rate for a measured time. The loss in weight of the cylinder was taken as the amount of gas passed, and this value agreed well with the result obtained by condensing the effluent gas and then expanding it to a known volume, pressure and temperature, and applying the ideal gas laws. The hydrogen flowmeter was calibrated by passing hydrogen through it at a fixed rate for a definite time and measuring the amount of effluent hydrogen both by passage through a wet-gas test meter and by displacement of water from a volumetric flask. A similar procedure was used for nitrogen. In the calibrations the exit pressure was one atmosphere; minor corrections for daily variations in atmospheric pressure were disregarded. Smooth calibration curves were drawn from a large number of points obtained on widely separated days. It is felt that the calibrations were accurate to ±2%.

The mercury-filled escape valve, 3, served the dual purpose of giving advance warning of developing plugs and of venting excessive pressures to the atmosphere, thus preventing damage. Used in conjuction with a barometer, the escape valve also served as a manometer.

Among the interchangeable reactor tubes at 4 were Pyrex glass tubes sixteen inches long over-all fitted with standard taper ground joints. The tubes had diameters as follows: A, $^1/_4$ in.; B, 1 in.; C, $^1/_2$ in. Reactor tube D was a one-inch diameter ordinary carbon steel tube with welded Fernico ends sealed to ground joints by means of graded seals. The metal reactor was carefully freed of oxide by pickling and rinsing thoroughly in absence of air prior to use. All reactor ground joints were air-cooled during operation of the system. Taking a ten-inch section of these tubes as the effective reactor length gave effective reactor volumes of 69 ml., 94 ml., 22 ml. and 131 ml. for tubes A, B, C and D, respectively.

For reactor tubes B and C the heating element was a movable tubular aluminum furnace with resistance wire wound over ten inches of its length and with the ends glass wool-insulated. Tubes A and D were lagged and wound with resistance wire directly over ten inches of their length. The temperature in all four tubes was measured with a silicone-insulated thermocouple whose junction was located at the center of the heated zone between the outside wall of the reactor tube and the heating element. During a run the temperature was maintained constant to ±2° by means of a Bristol pyrometer controller. The temperature distribution along tube A was determined by probing with a thermometer. Under static conditions at 200° it was found that the center six inches of the effective reactor length was within 5° of the indicated temperature while the center eight inches was within 15° of the indicated temperature. Under conditions of 350 ml./min. nitrogen flow and 200°, the temperatures were not excessively lowered.

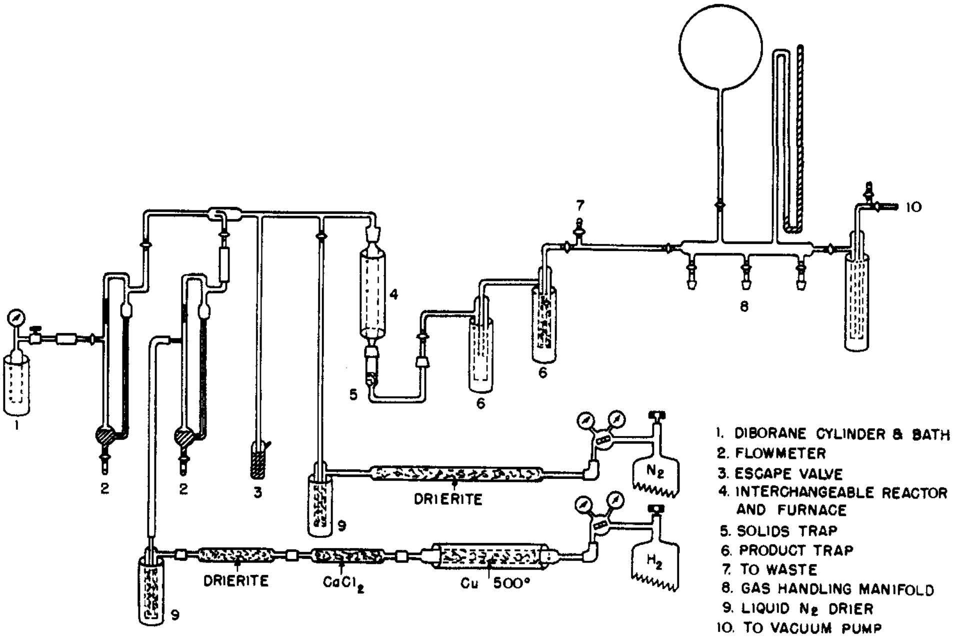

Fig. 1.—Single-pass system for thermal conversion of diborane–hydrogen mixtures.

The solids trap, 5, was a fine glass wool plug inserted in the line to remove the fluffy solid boron hydrides from the product stream.

The product traps, 6, were of conventional design. The second was packed with stainless steel helices to improve heat transfer and thus promote complete condensation.

The gas handling manifold, 8, was equipped with a manometer and with a storage and measuring bulb.

Stopcocks and ground joints in the system were lubricated with Apiezon greases. Slight browning of the lubricant indicated some reaction with boron hydrides; however, this was a negligible source of error and regreasing was unnecessary during extended periods.

Operation.—The following is best used in conjunction with the drawing of the system, Fig. 1, and with the description of the apparatus in the preceding section.

The diborane flowmeter was dried thoroughly by evacuation and filled with diborane. To avoid contamination by traces of hydrolysis products, the flowmeter was kept full of diborane during subsequent calibration, operation and intervening intervals. The short Neoprene sleeve used to attach the diborane cylinder to the flowmeter was flushed with dry nitrogen each time before attachment. The other flowmeter with attached hydrogen purifying train was flushed thoroughly with hydrogen and left filled with this gas continuously except for the one run in which nitrogen was used instead of hydrogen.

Prior to a run the apparatus was dried by evacuation, filled with nitrogen, and then opened to the atmosphere. With furnaces at temperature and cooling baths in place, the hydrogen flow was started and regulated by means of a reducing valve and a needle valve. The diborane feed was started and regulated by reducing the cylinder pressure to two atmospheres with solid CO_2 cooling and throttling the flow with a needle valve.

The amount of diborane used was determined by weighing the cylinder to one centigram before and after each run. Generally this quantity was 1.2–2.5 g. or 1.5–3.0 liters of gas. The time of each run, measured with a wrist watch, varied from 15 min. to 2 hr. depending on the flow rate.

As the run progressed, solid boron hydrides collected in the solids trap, the volatile boron hydrides condensed in the product traps and the hydrogen was vented to the atmosphere. Under conditions giving high conversions, the development of plugs in the solids trap caused premature shutdowns. Plugs occasionally occurring in the first product trap were relieved by removing the cooling-bath to melt them.

Upon completion of a run the diborane feed was first stopped, and after a few minutes the hydrogen flow was discontinued. Then the system was evacuated over 5–10 minutes. After the reactor tube was cooled with a stream of air, this part of the system was closed off from the product traps and disassembled for solids removal. The weight of solids was obtained by weighing the reactor tube and solids trap to one centigram before and after the run. On several occasions the yellow solids inflamed spontaneously after exposure to the atmosphere for a few minutes. Most of the fluffy yellow solids were collected between the lower end of the reaction zone and the glass wool plug. A small amount of solid boron hydrides escaped the solids trap and appeared in the first product trap. Varying quantities of dark solids, depending on conditions, occurred in the reaction zone. Reactor tube and solids trap were cleaned with aqueous ethanol for subsequent runs.

The volatile materials condensed in the product traps were distilled in vacuum to a bulb on the gas-handling manifold and analyzed as indicated above. Samples were stored in liquid nitrogen in bulbs equipped with two stopcocks to preclude air leakage and consequent violent reaction.

To reduce the time required for analysis in the Podbielniak still, many of the samples were first freed of the greater part of the unreacted diborane by warming them slowly to −80° and allowing the diborane to expand into a known volume at a measured temperature and pressure.

The diborane so removed was analyzed by determination of its gas density to a precision of less than 1%. The 200-ml. bulbs were calibrated with dry, carbon dioxide-free air; a check against diborane gave values less than 1% high. The molecular weights of recovered diborane were a maximum 3% high and an average 2% high. The high values were not due to absorption of boranes by the lubricant of the bulb's stopcock. Rather were they probably due to presence of higher boron hydrides. Comparison runs showed that no appreciable amounts of tetraborane were lost in the removal of diborane prior to distillation. Calculation of the "topped" diborane contaminant as pentaboranes would change the combined yield of these compounds by about five percentage points. It is felt that such an error would not be serious. Moreover, it should be noted that any errors of this type would be on the conservative side.

Results.—Detailed data for all the runs made are listed in Table V, while in Table VI may be found runs selected for comparison of the effect of temperature, residence time and amount of added hydrogen on conversion and yields.

A number of the headings in the tables require further consideration: (a) the time in seconds, or *residence time*, is a measure of the time that the reacting molecules were exposed to the reaction temperature. The figure was obtained by dividing the feed rate (ml. STP per second) into the volume (ml.) of gas at STP contained in the effective reactor volume under reaction conditions. (b) Deviations of the volumes of added hydrogen from the integers 1 and 5 were inadvertent. (c) Conversion is the per cent. of diborane which reacted; that is, it is the per cent. of starting diborane which was not recovered as diborane. (d) The yields of higher boron hydrides are based on the diborane which was converted. Thus if one were to feed 1000 ml. of diborane to the reactor and obtain from it 500 ml. of diborane and 200 ml. of pentaborane, the conversion would be 50% and the yield of pentaborane would be 100%. (f) The number under "solids and losses" may be taken as the yield of solid boron hydrides because the losses, mostly 2–10%, appeared to be due mainly to escape of solid boron hydrides from the solids trap into the first product trap.

The detailed data of Table V bring out a number of interesting points:

The pyrolysis of diborane appears to be an exothermic reaction. In runs 13 and 14 the temperature crept upward in spite of the fact that the current to the heating element was decreased.

Comparison of runs 15 and 21 indicates that addition of five volumes of nitrogen to the starting diborane has about the same influence on the extent and course of the pyrolysis as does the addition of one volume of hydrogen.

It may be seen from runs 16 and 17 that use of commercial, electrolytic tank hydrogen did not increase the formation of solids and that it is doubtful that any deleterious effects were encountered.

Table V

		Conditions			Yields, %				
Run	Reactor	Temp., °C.	Time, sec.	Volumes added H_2	Conversion	B_4H_{10}	B_5H_9	B_5H_{11}	Solids and losses
1	A	200	17	1.0	34	3	48	7	42
2	A	200	55	1.0	56	<1	43	0	57
3	A	227	17	0.0	66	<1	35	0	65
4	A	227	16	1.1	57	<1	48	0	52
5	B	225	14	5.0	27	2	69	0	29
6	B	220	15	4.7	23	2	64	7	27
7	B	250	15	1.0	85	0	28	0	72
8	C	225	3.0	0.0	40	3	42	8	47
9	C	225	3.3	0.0	36	3	39	13	45
10	C	225	3.2	0.0	36	3	39	13	45
11	C	225	3.1	1.0	26	5	53	15	27
12	B	225	3.0	5.5	7	25[a]	65	0	10
13	C	250-260	2.8	0.0	75	0	34	0	66
14	C	250–260	3.0	0.0	70	0	35	0	65
15	C	250	3.0	1.0	61	0	47	0	53
16	B	250	2.8	5.3[b]	21	2	65	3	30
17	B	250	3.0	4.7	28	1	57	6	30
18	C	250	2.9	4.9	31	2	65	0	33
19	D	240	3.2	5.9	14	5	67	13	15
20	B	260	2.8	4.2	43	1	61	0	38
21	C	250	3.0	4.5[c]	61	<1	46	0	54

[a] This material boiled at −55 to −35° at 90 mm. [b] Unpurified tank hydrogen was used. [c] Tank nitrogen purified by passage over copper at 500° was used.

Table VI

Selected Runs

Residence time, 15 sec.

	Volumes added H_2	Conversion	B_4H_{10}	B_5H_9	B_5H_{11}	Solids	Run
200°	1	34	3	48	7	42	1
225°	0	66	<1	35	0	65	3
	1	57	<1	48	0	52	4
	5	27	2	69	0	29	5
250°	1	85	0	28	0	72	7

Residence time, 3 sec.

	Volumes added H_2	Conversion	B_4H_{10}	B_5H_9	B_5H_{11}	Solids	Run
225°	0	36	3	39	13	45	9
	1	26	5	53	15	27	11
	5	7	25?	65	0	10	12
250°	0	70	0	35	0	65	14
	1	61	0	47	0	53	15
	5	31	2	65	0	33	18

Consideration of runs 17 and 18 leads to the conclusion that alterations in reactor dimensions may influence the reaction by affecting the rate of heat flow to the gas. Thus with the larger diameter tube an appreciable amount of dihydropentaborane appeared in the product probably because of a lowered average gas temperature. Run 20 shows how this undesirable change may be compensated by a small variation in temperature of the reactor shell. Runs 5 and 6 also show how a small change in temperature can prevent the appearance of dihydropentaborane in the product. That this same result may be obtained by lengthening the residence time is shown by runs 1 and 2.

It is evident from run 19 that an ordinary carbon steel reactor is suitable for the thermal conversion of diborane–hydrogen mixtures. The lowered conversion and increased amounts of tetraborane and dihydropentaborane may be attributed to the lower temperature and larger reactor used.

Discussion

While the isolation of pentaborane from the products of the pyrolysis of diborane is not new, the synthesis in good yields and free of dihydropentaborane is advantageous since the boiling points at 100 mm. pressure are only 4° apart. Obviously the problem of purification by distillation is considerably simplified if the undesirable dihydropentaborane is minimized. From the data presented it is fairly clear that there is no one set of reaction conditions that can be considered ideal for the synthesis of pentaborane. Rather there is a range in which temperature can be exchanged for reaction time, and almost identical results will be obtained. A comparison of the data at 225° and 15 sec. residence time with that at 250° and 3 sec. residence time in Table VI illustrates this point nicely.

In view of Schlesinger and Burg's work[5] and the results of this paper there can be little doubt that hydrogen does aid in obtaining better yields of pentaborane from diborane. When the stoichiometry of the reactions is considered, it is surprising that pentaborane should be favored since more hydrogen is released when it is formed than when dihydropentaborane is made. Whatever the mechanism of the synthesis of pentaborane, it is almost certainly irreversible. The eventual destruction of pentaborane that is observed at higher temperatures or too long reaction times is probably not a reaction of pentaborane with hydrogen, but rather a reaction between diborane and pentaborane to yield higher hydrides.[8]

The irreversibility of the formation of pentaborane should not be interpreted as meaning that hydrogen has no effect upon the rate of decomposition of diborane. The data of Table III and Table VI make it abundantly clear that the rate of decomposition of diborane is inversely proportional to some function of the hydrogen pressure.

No serious attempt was made to synthesize dihydropentaborane, but certain conclusions can be drawn which substantially agree with the experiments reported by Stock and Mathing.[5] From Table I it is easily seen that relatively lower temperatures are desirable, and from Table IV that shorter residence times are advantageous. Since the rate of production of dihydropentaborane is relatively small at these lower temperatures, a circulating gas system is almost a necessity for its

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[8] Schlesinger and collaborators, unpublished results at present contained in reports to various government agencies and in University of Chicago doctoral theses.

synthesis. Hydrogen does not seem to help the synthesis of dihydropentaborane.

The choice of a circulating or single pass system for making pentaborane depends mostly upon how much diborane is available for the job. If relatively small quantities are on hand, a circulating gas system will utilize the material most efficiently. On the other hand, if diborane is considered expendable, a single pass system is so much easier to build that this method will be preferable.

Acknowledgment.—The authors would like to express their gratitude to Dr. Arthur E. Newkirk for his many helpful suggestions.

RECEIVED JUNE 15, 1950

[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO]

Low Temperature Oxidation of Copper. II. Reaction Rate Anisotropy[1]

BY T. N. RHODIN, JR.[2]

The oxidation rate of single crystal copper surfaces exposed to pure oxygen at low temperatures from 78 to 323°K. has been observed to be highest for the least densely packed (100) face and smallest for the most densely packed (111) face. The rate anisotropy is adequately described by the mathematical treatment of Mott and Cabrera although the physical significance of their assumptions is ambiguous. The reaction rate anisotropy was also shown to be consistent with the theoretical requirements of Frank and Van der Merwe for the existence of oriented overgrowths. According to their model, pseudomorphic oxide structures may account for the oxidation rate anisotropy.

Introduction

There are at least two important aspects to the manner in which reaction potentials on a given metal surface are affected by surface structure in the formation of protective oxide films.

First, the chemical activity of the metal surface is dependent on the atomic spacing and geometry of the surface atoms. Second, the mechanical properties of very thin oxide films that form in the initial stages of attack, such as permeability and cohesion, are influenced by the short range forces of the underlying metal.

It is desirable to evaluate the reactive nature of metallic oxide films on the basis of fundamental considerations of this type. Should these fundamental considerations of thin oxide film formation at low temperatures prove valid, they promise to be of importance in understanding oxidation phenomena under more general conditions. There is reason to believe that similar considerations valid at higher temperatures can be evaluated on the basis of the less complicated oxidation effects observed at low temperature. Single crystal copper surfaces in oxygen atmospheres at low temperatures were systematically studied from this viewpoint.

Procedure and Materials

Single crystals of copper suitable for surface studies have been successfully prepared and characterized.[3a,3b] The physical mechanism of formation of very thin oxide films at low temperatures has also been evaluated in some detail on both a theoretical[4a,4b] and experimental basis.[5a,5b] The orientation relationships existing between copper and cuprous oxide have been thoroughly investigated and confirmed.[6] The energetics involved in the formation of oriented over-growths have also been considered in some detail.[7a,7b] Finally the vacuum microbalance has been shown to be a powerful tool in the study of the surface chemistry of small surfaces.[8a,8b]

The samples were electropolished single crystal plates of copper (0.5″ × 0.75″ × 0.005″) sectioned from a large single crystal grown in a standard Bridgman manner. The copper was vacuum cast to a purity of 99.995% with iron and aluminum chief remaining impurities determined by spectrochemical analysis. Considerable efforts were made to define the surface crystallography and roughness on an atomic scale and true surface areas were determined using a specially developed differential adsorption technique. The criteria by which the crystallography and flatness of the surface on a microscale were evaluated are described in detail elsewhere.[8b] It is believed that the surfaces of this study are essentially flat on a molecular scale and that the surface arrangement of the atoms is approximately that of a known undistorted crystal face.

The oxidation kinetics were followed with a sensitive vacuum microbalance previously described[9] with which weight changes as small as 10^{-7} g. were determined with an accuracy of ±20%. The average oxide film thickness was calculated from weight changes in the usual manner assuming the formation of cuprous oxide except that the true surface areas were known in this study and the average true surface areas before and after oxidation were used in order to obtain a more precise value for the average oxide film thickness.

The uptake of oxygen by the surface was measured in the time range from 5 seconds to 1 month for eight temperatures in the range 78 to 323°K. on each of two samples for each of the three major crystal faces (100), (110) and (111). The weight changes reported here correspond only to that fraction of the oxygen uptake which was not outgassable at 500°K. These values were independent of oxygen pressure in the range 10–100 mm. The temperatures were determined with a chromel–alumel thermocouple mounted in a dummy plate identical in shape, size and material to the sample hanging on the balance. The other techniques for maintaining and measuring vacuum conditions were not especially improved over those previously described.[8a,8b] Although the edge area was reduced to a minimum (<0.1% total area) localization of the reaction at the edges is possible to some extent. It is believed, however, that selective edge attack is more likely at high temperatures. This effect at low temperatures is considered to be a minor one because extended oxidation at much higher temperatures (>300°) showed no evidence of non-uniform oxidation.

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[1] This research was supported in part by Army Air Forces Contract AF-33(038)-6534.

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