

persion which is optically void on heating to 55°. The apparent  $DP_n$  in chloroform was found to be 1050 at 30°. The effect was even more pronounced in the case of corn amylopectin acetate (fraction not precipitated by Pentasol). During acetylation of this fraction, the reaction mixture set to a gel when the ratio of carbohydrate to pyridine plus acetic anhydride was 2 to 100 and it was necessary to reduce this ratio to 1 to 100 in order to obtain a fluid medium and to complete the acetylation. The triacetate remained insoluble, for the most part, even with prolonged boiling in chloroform or mixtures of chloroform and alcohol. However, it was found that corn amylopectin subfraction III<sup>16</sup> forms a triacetate which dissolves in chloroform and for which a  $DP_n$  value of 635 was found. The acetates of subfractions of higher molecular weight were only partially soluble. These experiments leave no doubt of the very great association which can exist between these carbohydrate molecules (or molecular entanglement), particularly in very high molecular weight ranges and which may operate to some extent even in the low molecular weight ranges.

The reluctance of carbohydrate derivatives to disperse molecularly in organic solvents leaves open to question the results of all physical measurements of molecular weight which involve a study of solutions whether the method consists of osmotic pressure, viscosity, light scattering or sedimentation measurements. It is believed that the extent of dissociation depends not only on the solvent which is employed but possibly also on the temperatures used and on the type of starch derivative, and that these considerations explain

in part at least the wide spread in values reported in the past for the chain length of corn amylose.

For the present in fundamental studies it would seem wise to adopt the use of a readily prepared derivative, such as the acetate, and a solvent such as chloroform which gives a low order of molecular weight values by osmotic pressure measurements and a definite procedure in respect to temperature and time, until these values can be checked by a completely independent method. Boiling temperatures are suggested for preparing the solutions and 30° for measurement.

### Conclusions

The apparent  $DP_n$  values for the acetates of corn amylose and its subfractions have been calculated from osmotic pressure determinations using selected solvents. Of those used, chloroform gave the lowest  $DP_n$  values; the acetate of one corn amylose sample prepared by Pentasol precipitation was found to have a  $DP_n$  of 455 and another 495. The acetate of a butanol precipitated corn amylose had a  $DP_n$  of 435. Subfractions of the latter varied in  $DP_n$  between 250 and 675.

Higher values for  $DP_n$  were found in other solvents tried and this may be explained as being due to association of the acetates in these solvents. Starch acetate samples tend to become visibly insoluble, or partly insoluble in organic solvents as the  $DP$  exceeds that of corn amylose. Tapioca amylose acetate appeared to be very nearly the limit in respect to molecular size for solubility in chloroform and showed a  $DP_n$  of 1050 in this solvent.

ARGO, ILLINOIS

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

## The Preparation of Boron Hydrides by the Reduction of Boron Halides

BY DALLAS T. HURD

It recently (1945) has been found that boron hydrides, specifically diborane and diborane monohalides, can be synthesized by the reduction of boron halide vapor with hydrogen in the presence of metals<sup>1</sup> at elevated temperatures.

In addition it has been discovered that the hydrides of the alkali and alkaline earth metals will reduce gaseous boron halides to diborane at temperatures above about 200°.<sup>2</sup>

### Experimental

**A. Reductions Involving Metals.**—1. Boron trichloride gas<sup>3</sup> and hydrogen in *ca.* 1:3 ratio were passed through

(1) A general criterion for the metal is that it be more electropositive than boron.

(2) Mention should be made of the reactions in ether solution between boron halides and the hydrides of electropositive metals to yield boron hydrides discovered by H. I. Schlesinger and his co-workers at Chicago, Ill.

(3) Boron trichloride supplied by the Cooper Metallurgical Laboratories, Cleveland, Ohio; purity over 98%.

a vertical bed of -20 mesh aluminum granules in a 1" Pyrex tube heated to 350°. After a short induction period aluminum chloride was observed subliming out of the reaction zone and the gas issuing from the reactor became spontaneously inflammable, burning with a green flame.

Chemical tests on samples of the exit gas indicated the presence of boron hydrides. These included the standard tests such as the decolorization of hanging drops of permanganate solution, formation of chocolate brown precipitate on paper soaked in silver nitrate solution, formation of hydrogen bubbles in hanging water droplets, as well as other chemical reactions characteristic of the boranes. The exit gas gave negative results on all of these tests until the temperature necessary for reaction had been reached.

To study the reaction in more detail a larger apparatus was designed (Fig. 1) comprising a reactor tube 2½ in. in diameter, heated in a cylindrical furnace, followed by a trap to collect the aluminum chloride formed during the reaction and by traps at -80 and -190° to collect the reaction products. The side arm leading from the reactor to the aluminum chloride trap was kept warm electrically to avoid deposition of the halide in the tube. The boron chloride and hydrogen were metered in through rotameters, the hydrogen being purified in a conventional set-up. The

reaction temperature was followed by a thermocouple embedded in the charge of aluminum.

Upon distillation of the condensed products following a run it was observed that the material in the trap at  $-190^\circ$  was mostly diborane together with some hydrogen chloride. The greater portion of the boron hydride was collected at  $-80^\circ$  as diborane monochloride ( $B_2H_5Cl$ ) along with excess boron trichloride. Hydrolytic analyses of the distillation fraction boiling at  $-92.5^\circ$  established the identity of the principal reaction product as diborane.

A number of experiments were made in this and in similar but smaller apparatus with various ratios of gaseous reactants and at temperatures ranging from  $300$  to  $500^\circ$ . Representative data are tabulated in Fig. 2. The products initially were analyzed by slow distillation in a Podbielniak automatic still at atmospheric pressure.<sup>4</sup> (With this procedure the unstable diborane monochloride is decomposed into diborane and boron chloride during the distillation.) Later a method for determining the amount of diborane by direct hydrolysis of samples of the exit gas was employed.

In no case were the higher hydrides of boron found in the condensed products in amounts sufficient to be detected. There was evidence, however, that small quantities of solid boranes such as  $B_{10}H_{14}$  were caught in the first trap along with the aluminum chloride.

The reaction apparently did not proceed at temperatures much below about  $300^\circ$ .

Upon removal of the tube from the furnace following a reaction, the granular aluminum charge frequently was found to be coated with a dark blue deposit. This blue deposit, readily soluble in dilute hydrochloric acid, conceivably may be connected with the mechanism of the reaction as an active intermediate since its character and amount did not seem to change with variation of the reaction time even in long runs where channeling of the charge due to removal of aluminum would occur. The rapidity with which the aluminum was dissolved by dilute hydrochloric acid indicated also that the usual oxide coating on the metal had been removed by the reaction.

Several analyses of used reactor charges were made by dissolving weighed samples in hydrochloric acid and weighing the insoluble residue as free boron. These indicated that only a very small percentage of the boron trichloride passing through the reactor was lost by reactions to form free boron. Except in the runs at very high temperatures where as much as 5% loss might be encountered, the amount of free boron generally was less than 1%.

Material balances on a number of the runs showed that in general the over-all loss of boron in the reactor was quite low. For example, 18 g. of boron trichloride together with hydrogen in 1-6 mole ratio was charged to the reactor at  $360^\circ$  during the extraction of a sample from the portion of the run measured. This amount of boron chloride is equivalent to 1.66 g. of boron. Collected in the sample trap was 13.5 g. of boron trichloride and 0.47 g. of diborane (after distillation) representing an amount of boron equal to about 1.60 g.

It was found advantageous to purify and dry the hydrogen used, not from any marked improvement in the reaction as a result, but because it avoided the plugging of lines and loss of material resulting from the hydrolysis of boron trichloride to boric oxide by traces of water.

Several types of aluminum were tried with no marked difference in performance except for a general increase in the conversion with the surface area of the metal. With very fine material, however, channeling and a resulting loss of contact area was encountered.

2. Magnesium, zinc and sodium (molten) behaved similarly toward mixtures of boron trichloride and hydrogen although the first two gave poorer yields than aluminum. There is reason to believe, however, that with a suitable method of providing contact between molten sodium and the gaseous reactants, good yields of diborane could be obtained.

3. Boron trifluoride and hydrogen in about 1:2 ratio were passed through heated magnesium powder. At

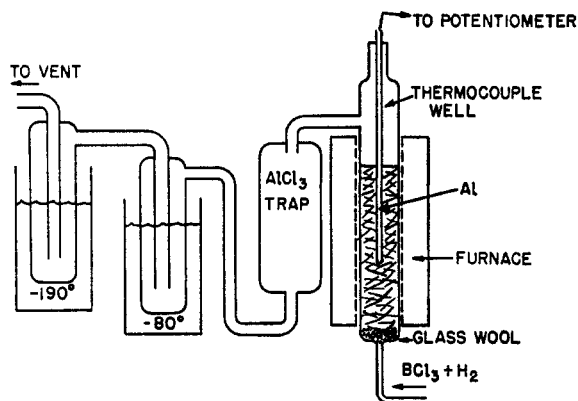


Fig. 1.—Diborane apparatus.

about  $375^\circ$  a violent reaction ensued and the temperature of the charge rose rapidly. Small amounts of diborane were detected in the exit gas and some of this material was condensed and distilled. Upon completion of the experiment it was seen that the reaction must have been very exothermic since the charge was blackened and local overheating had warped the glass of the reactor tube. This very vigorous reaction and low yield also were encountered in trying to produce reaction of boron fluoride and hydrogen over aluminum.

4. An experiment in which hydrogen was bubbled through boron tribromide at  $25^\circ$  and into a charge of granular aluminum at  $250^\circ$  produced aluminum bromide and small amounts of diborane. The yield was not high in the one reaction attempted.

**B. Reductions with Metal Hydrides.**—1. A charge of powdered sodium hydride<sup>5</sup> was placed in an inclined  $1^\circ$  Pyrex tube and a mixture of boron fluoride and hydrogen in ca. 1:2 ratio was passed through the charge while the temperature gradually was increased. At about  $180^\circ$  boron fluoride disappeared entirely from the exit gas and the presence of considerable quantities of diborane was confirmed. It later was shown that the presence of hydrogen was necessary to sweep the diborane product out of the hot zone to avoid pyrolysis. An experiment using nitrogen in place of hydrogen gave similar results so it is questionable whether either gas had any direct effect on the reaction.

The reaction was halted by the plugging of the reactor tube and it was found upon opening the furnace that much of the gray sodium hydride had been changed to a white salt, presumably either sodium fluoride or sodium borofluoride. No perceptible darkening of the charge which might indicate the deposition of free boron was observed.

Although no quantitative data as to the conversion of boron fluoride to diborane were obtained it seems quite likely, considering the total disappearance of boron fluoride from the exit gas, the amount of diborane produced, and the absence of pyrolysis products in the reactor, that the yield was high. With a suitable method of contacting gases with solids this method for the preparation of diborane may be of interest. There is the possibility, however, depending upon the reaction conditions, of losing boron fluoride by converting sodium fluoride to sodium borofluoride.

2. Boron trichloride and hydrogen passed through a charge of powdered sodium hydride at  $200$ – $220^\circ$  reacted to produce diborane in the exit gas and sodium chloride in the charge. Both of these materials were identified by chemical tests. Boron trichloride alone passed rapidly over heated sodium hydride gave faint tests for diborane in the exit gas but the reaction was very exothermic and much darkening of the charge was noted. In all of these runs the tubes plugged quite rapidly due to build-up of sodium chloride in the charge.

(5) Sodium hydride generously supplied by the du Pont Electrochemicals Dept., Niagara Falls, N. Y.

(4) Distillation analyses were made by Dr. L. V. McCarty.

Boron trichloride and hydrogen also reacted with crushed calcium hydride to produce spontaneously inflammable gaseous products which responded to the conventional tests for diborane. Calcium chloride was formed in the charge.

3. It is of interest to note in passing that some chemical evidence has been obtained for the formation of boron hydrides in the violent reaction that ensues upon heating mixtures of powdered anhydrous boric oxide and lithium hydride or sodium hydride. This hardly seems desirable as a preparative method, however.

### Discussion

It indeed appears surprising that a substance as thermally unstable as diborane can be synthesized under conditions that ordinarily would result in a rather rapid pyrolysis of this material. Several factors, however, may explain why so little pyrolysis actually does occur and why the losses of boron are small.

The actual contact time during which a unit of gas remained at elevated temperatures was in most cases rather short (Table I). This would tend to minimize pyrolysis losses. Also, there generally has been present in the reaction zone a large excess of hydrogen over the amount actually needed for the formation of boron-hydrogen com-

pounds. Although the effect of hydrogen in inhibiting the decomposition of hydroborons at room temperature is well known, it well may be that this effect is not operative at elevated temperatures and the hydrogen may be effective largely by diluting the diborane product.

In addition it may be possible that more stable monoboron compounds, *e. g.*,  $\text{BHCl}_2$ ,  $\text{BH}_2\text{Cl}$ , may be the primary products of a stepwise reaction and that these transient compounds later undergo rearrangement into diborane and boron trichloride when out of the reactor hot zone.

In the runs where boron fluoride was used no inflammation was noticed even though large quantities of diborane were present at times in the exit gas. This may indicate either that diborane monofluoride ( $\text{B}_2\text{H}_5\text{F}$ ) is not formed in the reaction or is not spontaneously inflammable if it is formed.

Reasoning from the experiments with metal hydrides, the reduction of boron halides with hydrogen over metals similarly may appear at first glance to involve the initial formation of reactive hydrides on the surface of the metal followed by replacement reactions. There is, however, little direct evidence to support this over other possible mechanisms, and at the present time the exact nature of the reaction is not known.

### Summary

Diborane and diborane monohalides have been produced by the reduction of boron halides with hydrogen over active metals at elevated temperatures.

The reaction of gaseous boron halides with active metal hydrides also has been found to produce diborane.

SCHENECTADY, NEW YORK

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TABLE I  
DIBORANE PREPARATIONS

| T,<br>°C. | $\text{H}_2$ /<br>$\text{BCl}_3$ | C. T. <sup>a</sup> | Al <sub>2</sub> Si <sub>2</sub> | Condensed product,<br>mole per cent. |     |                | Conver-<br>sion,<br>% <sup>b</sup> |
|-----------|----------------------------------|--------------------|---------------------------------|--------------------------------------|-----|----------------|------------------------------------|
|           |                                  |                    |                                 | $\text{B}_2\text{H}_6$               | HCl | $\text{BCl}_3$ |                                    |
| 1 360     | 4-1                              | 5"                 | -12                             | 2.9                                  | 4.1 | 93             | 6                                  |
| 2 320     | 3-1                              | 12"                | -40                             | 3.5                                  | 1.3 | 95.2           | 6.7                                |
| 3 350     | 3-1                              | 12"                | -40                             | 5.8                                  | 0   | 94.2           | 11                                 |
| 4 350     | 6-1                              | 15"                | -40                             | 8.8                                  | 1.7 | 89.5           | 16.4                               |
| 5 475     | 6-1                              | 6"                 | -30                             | 12.4                                 | 1.7 | 85.9           | 20.4                               |
| 6 500     | 6-1                              | 4"                 | -30                             | 6.7                                  | 0.9 | 92.4           | 12.5                               |
| 7 450     | 6-1                              | 6"                 | -30                             | 17.2                                 | 3.9 | 78.9           | 30                                 |

<sup>a</sup> C.T. Calculated contact time in hot zone, 1" dia. reactor. <sup>b</sup> Per cent.  $\text{BCl}_3$  converted to  $\text{B}_2\text{H}_6$ , assuming no boron loss in the reactor.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## Liquid-Liquid Solubility of Perfluoromethylcyclohexane with Benzene, Carbon Tetrachloride, Chlorobenzene, Chloroform and Toluene

By J. H. HILDEBRAND AND D. R. F. COCHRAN

The extraordinary solvent properties of fluorocarbons which have come to light during the last few years have been considered in two recent papers from this Laboratory, one by R. L. Scott,<sup>1</sup> who gave "solubility parameters" for a number of fluorocarbons and showed their general harmony with available solubility data, and another by Benesi and Hildebrand<sup>2</sup> who reported a figure for the solubility of iodine in normal perfluoroheptane at 25° and showed that the remarkably small solubility, only 0.007 the solubility in an ideal solution, does not overstrain existing solubility theory

for regular solutions.<sup>3</sup> This instance of the adequacy of theory to cope with an extreme departure from Raoult's law encouraged us to measure other fluorocarbon solubilities in the expectation that they would have much more than merely empirical value and could be used in connection with refinements in the general theory.

The large molal volumes of the fluorocarbons compared with the corresponding hydrocarbons leads to unusually low "internal pressures" or "cohesive energy densities," while their high

(1) R. L. Scott, *THIS JOURNAL*, **70**, 4090 (1948).

(2) H. A. Benesi and J. H. Hildebrand, *ibid.*, **70**, 3978 (1948).

(3) Cf. J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," 3rd edition, 1949, Reinhold Publ. Corp., New York N. Y.