The above reaction mechanism can, therefore, be regarded only as a possible way of representing the initial processes.

If the usual steady-state approximation is applied to this mechanism, the rate equation becomes

$$\frac{-\,\mathrm{d}[\mathrm{B_2H_6}]}{\mathrm{d}t} = \frac{2k_2\sqrt{K}(k_4/k_3)[\mathrm{B_2H_6}]^{5/2}}{(k_4/k_3)[\mathrm{B_2H_6}] + [\mathrm{H_2}]}$$

This reduces to the experimental equation if we replace $[B_2H_6]$ by $p = xp_0$, substitute for $[H_2]$ the expression $p_0 - p = (1 - x)p_0$ (which implies 1 mole H_2 per mole diborane reacted), and let $k_4/k_3 = 1$. It would of course be possible to treat k_4/k_3 as an adjustable constant, and to take a more realistic value of $[H_2]$, but the other uncertainties would hardly justify such refinements.

Following this procedure, the experimental constant k' is identified with the coefficient $2k_2\sqrt{K}$. The corresponding experimental activation energy, E', is interpreted as $E_2 + {}^1/_2\Delta H_1^0$. In order to estimate this quantity, values of the rate constant at a series of temperatures were selected and the customary plot of log k' against $1/T$ was prepared. Values are given in Table III. A good straight line is obtained whose slope yields the value 26000 cal./mole for E'. Granting that E_2 is probably small, the value of ΔH_1^0 becomes of the order of 50000 cal./mole, which seems not unreasonable.

TABLE III

VARIATION OF RATE WITH TEMPERATURE

Temp., °C.	Rate constant[a]
85.0	5.8×10^{-7}
103.4	2.8×10^{-6}
121.8	1.2×10^{-5}
140.3	7.5×10^{-5}
163.5	3.5×10^{-4}

[a] The units of the rate constant are mm.$^{-1/2}$ sec.$^{-1}$.

If the general outlines of this work are accepted, it may be concluded that the over-all process is in fact a radical-type addition polymerization complicated by quasi-reversible dehydrogenation. Thus in a formal sort of way the similarity of diborane to ethylene, which is indicated by some physical properties, is preserved in the kinetics.

PRINCETON, NEW JERSEY RECEIVED AUGUST 28, 1950

[CONTRIBUTION FROM THE GENERAL ELECTRIC CO. RESEARCH LABORATORY]

Kinetics of Pyrolysis of Diborane[1]

BY JOHN K. BRAGG, LEWIS V. McCARTY AND F. J. NORTON

The kinetic studies of the thermal decomposition of diborane reported here are of three kinds: First, the rate of increase of total pressure has been measured as a function of temperature and initial pressure. Three conclusions are drawn from the results: (1) the order of the rate controlling step is 1.5; (2) the reaction is homogeneous in glass; (3) the activation energy of the rate controlling step is 27.4 ± 0.7 kcal./mole. Second, the rate of formation of hydrogen has been measured. The results confirm the value 1.5 of the order, and indicate an activation energy of 25.5 ± 0.5 kcal./mole. The difference between activation energies is due to temperature effects on secondary reactions. Third, the mass spectrometer has been used to follow the reaction; in this way the concentrations of several participant species were measured. It is concluded (1) that the order of the step controlling the rate of disappearance of diborane is 1.5, (2) that dihydropentaborane (B_5H_{11}) is an intermediate in the formation of most other boranes from diborane, and (3) that the formation of pentaborane (B_5H_9) from dihydropentaborane is probably a simple first order step. The reaction scheme

$$\mathrm{B_2H_6} \rightleftarrows 2\mathrm{BH_3}$$
$$\mathrm{B_2H_6} + \mathrm{BH_3} \longrightarrow \text{intermediate products}$$
$$\text{intermediate products} + \mathrm{B_2H_6} \longrightarrow \mathrm{B_5H_{11}} + 2\mathrm{H_2}$$
$$\mathrm{B_5H_{11}} \longrightarrow \mathrm{B_5H_9} + \mathrm{H_2}$$
$$\mathrm{B_5H_{11}} \longrightarrow \mathrm{B_2H_6},\ \text{higher hydrides}$$

accounts satisfactorily for the observations of the mass spectrometer. The equations derived from it also account for the observed hydrogen pressure data, provided (a) a modification can be made to include a short-lived initial period of rapid hydrogen production, (b) m may be set equal to 6 in the step $5B_2H_6 \rightarrow$ higher hydrides $+ mH_2$. This would correspond to an "average" hydride composition of B_5H_9, although not necessarily in the *form* of B_5H_9 as demonstrated by the mass spectrometer. The equations also account for observed total pressure data, *provided* $m = 6$ *and* an average of one gas phase hydride molecule is formed.

Introduction

Work on thermal decomposition of the boron hydrides has been reported by Stock,[2] Burg and Schlesinger,[3] and Dillard.[4] A kinetic analysis of the decomposition mechanisms has not yet been presented.

In the present paper we report the results of three different experimental methods as applied to pyrolysis of diborane. In part II, studies of the rate of total pressure increase are described; in part III the results of an investigation of the rate of hydrogen formation are given. Part IV contains a study of the details of the decomposition as elucidated by the mass spectrometer.

Certain attempts to describe a reaction mechanism which gives sufficient correlation of the various observations are discussed in part V.

II. Rate of Pressure Increase

Experimental

Apparatus.—The apparatus centered about a Pyrex 211.8-cc. bulb, which served as a reactor, immersed in a

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[1] This work was done on Army Ordnance Contract TUI-2000.

[2] Stock, "Hydrides of Boron and Silicon," 1933, Cornell University Press; *Ber.*, **69**, 1456 (1936).

[3] Burg and Schlesinger, THIS JOURNAL, **53**, 4331 (1931); *ibid.*, **55**, 4009 (1933); *Chem. Revs.*, **31**, 13 (1942).

[4] C. R. Dillard, Doctoral Thesis, University of Chicago, 1949. We are indebted to Professor Schlesinger for making a copy of the thesis available to us.

thermostated (±0.1°) silicone oil-bath. The entrance to the reactor was a piece of 2-mm. capillary tubing which connected through a stopcock to a short vacuum line with a $^3/_8''$ mercury manometer. A stopcock from the vacuum line led to a pump and a take-off joint used to charge the reactor. When the latter stopcock was closed the volume of the system not in the oil bath, *i.e.*, at room temperature, was 20–30 cc.

Operation.—The reactor bulb was thermostated before gas was allowed to enter. At 0.2 min. after filling, the manometer and reactor were isolated from the diborane storage flask; at 0.5 min. after filling, the stopcock between reactor and manometer was closed so that the pressure in the reactor at this time could be read. This pressure was used to calculate the initial diborane concentration.

The stopcock between manometer and reactor was reopened after the reading, and closed and reopened for each subsequent measurement.

Materials.—The diborane was stored in stainless steel cylinders at −18°. Samples were removed to storage at liquid nitrogen temperature and vaporized therefrom immediately before use. Mass spectrograms indicated the material from the cylinders contained less than 1% of impurity. It was thought that subsequent vaporization from a liquid sample would produce material of sufficient purity for these experiments; however, at the start of several runs small irregularities were noted, the source of which was never accurately determined. (See discussion of materials in part III.)

Results and Discussion

Figure 1 is a plot of pressure against time for a typical run. Its general characteristics are common to all the runs; hence we have simply tabulated numerical data for runs at other pressures and temperatures. In many cases the discontinuity in rate, observed in Fig. 1 at 55 min., is not so sharp, and the part of the curve beyond the discontinuity shows a gradual decrease in rate. This discontinuity in rate does not seem to be exactly reproducible: that is, it has never failed to occur, but the time of occurrence apparently bears little relation to the pressure. The time of increased rate was observed to coincide with the onset of formation of yellow solids in the reactor, but decaborane, $B_{10}H_{14}$, was observed in small amounts before.

TABLE I

RATE OF PRESSURE INCREASE IN DIBORANE

Temp., °C.	Concentration mole/liter × 10^2	Rate of pressure increase, mole/liter/hour × 10^4
89.6	2.718	3.8
	2.092	2.7
	1.536	1.6
100.0	2.153	7.4
100.0	2.188	8.0
99.9	2.097	7.3
100.0	2.127 Glass-packed	7.4
100.0	2.142 Glass-packed	7.6
100.0	2.123 Fernico-packed	8.7
100.0	2.163 Fernico-packed	8.5
99.9	1.310	3.7
99.9	1.281	3.5
100.0	0.437	0.73
100.0	0.433	0.73
110.1	2.036	19.3
	1.275	9.3
	0.4334	1.9
120.1	0.6352	7.1
	.4191	3.1
	.2165	1.1
130.1	.4008	9.5
	.2119	2.9

TABLE II

THE ORDER OF THE B_2H_6 PYROLYSIS REACTION FROM THE PRESSURE RISE DATA OF FIG. 2

Temp., °C.	*n*	
89.6	1.52	1.49 av.
100.0	1.45	
110.1	1.49	
120.1	1.68	
130.1	1.89	

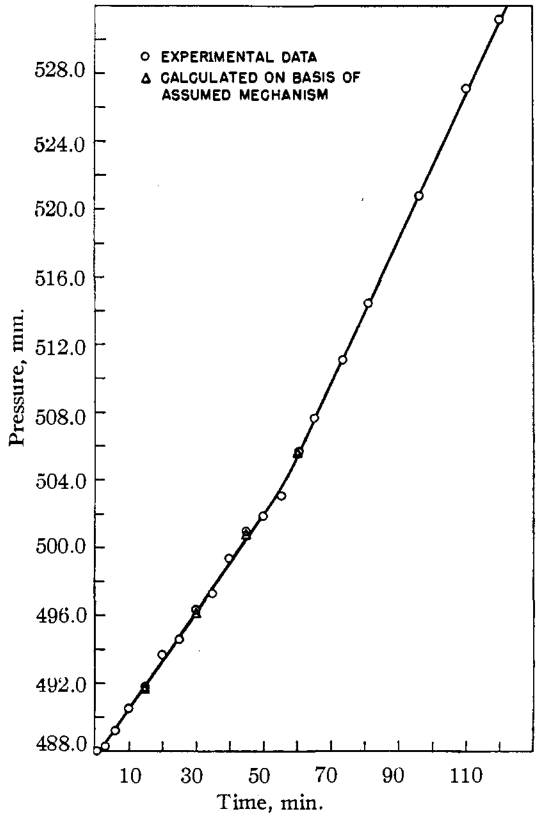

Fig. 1.—Rate of pressure increase in B_2H_6 (0.02097 mole/liter) at 99.9°.

In those reactors in which yellow solids were formed, the amount of the deposit was always greater in the lower part of the bulb. This indicates that most of it was formed in the gas phase. The presence of these solids in reactors used in further experiments after thorough evacuation did not influence the results noticeably.

From the rate of pressure increase *prior to* the discontinuity in rate, as given in Table I for various pressures and temperatures, one may calculate an "order" for the pressure increase: that is, the exponent in the expression

$$\text{rate of pressure increase} = kc_0^n$$

where c_0 is the initial concentration of diborane. The resulting values are given in Table II for the various temperatures.

At the higher temperatures *n* is seen to drift toward second order; only the first three figures show reasonable agreement. Because of the nearness of these numbers to 1.5, and because of other results to be detailed below, we believe this value is the correct expression of the actual state of affairs.

In Fig. 2 the rate of pressure increase is plotted against the 1.5 power of the initial diborane concentration. The rate constant can be obtained from the slope of such a plot; values obtained are given in Table III.

Table III

Rate Constants for Pressure Rise Dependence

Temp., °C.	k(liter/mole)$^{0.5}$/hour
89.6	0.085
100.0	0.240
110.1	0.66
120.1	1.31
130.1	3.6

A plot of $\log_{10} k$ against the reciprocal of the absolute temperature was drawn to weight the 89.6, 100 and 110.1° points most heavily. The activation energy so obtained is 27.4 ± 0.7 kcal./mole. If the 120.1 and 130.1° points are disregarded, the value obtained is 27.7 kcal./mole.

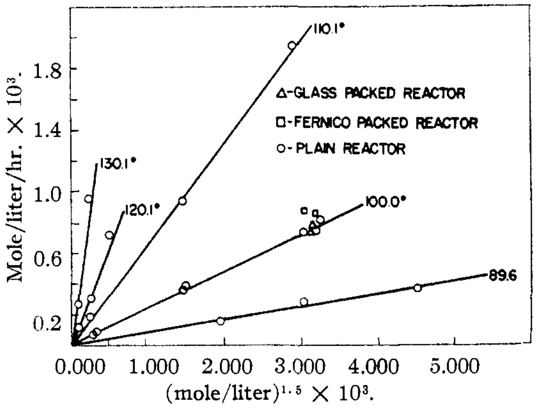

Fig. 2.—Rate of pressure increase in B_2H_6 *vs.* initial concn. raised to the 1.5 power.

Results obtained at 100° with two kinds of packed reactors are included in Table I. Glass-packed reactors contained short sections of Pyrex tubing, which corresponded to an increase in surface area over unpacked reactors of about 760%. The results given in Fig. 2 indicate that the reaction is homogeneous in glass vessels.

The Fernico packing was added to determine whether this metal, which is used in the mass spectrometer leak, would influence the reaction. The estimated surface of Fernico metal was 880 sq. cm. The data in Fig. 2 indicate a rate about 15% greater than for unpacked reactors. It must be emphasized that there is no such large amount of the metal in the mass spectrometer reactor.

III. Rate of Hydrogen Formation

Experimental

Apparatus and Operation.—Spherical 200-cc. Pyrex reactors were equipped with 1 mm. stopcocks and $^{12}/_{30}$ inner ground glass joints so that they could easily be removed from a thermostated (±0.1°) silicone oil-bath.

In operation a reactor was placed in the oil-bath and evacuated; then it was filled to the desired pressure (±1.2 mm.) from a diborane reservoir. After 0.2 min. the reservoir was shut off from the system, which now consisted of a mercury manometer and the reactor on a vacuum line. The reactor stopcock was closed at 0.5 min., and the pressure read from the manometer.

To stop the reaction, the bulb was removed from the oil-bath 0.04 min. before the recorded time, drained until 0.04 min. after this time, and then quenched in ice-water. After cooling the bulb in liquid nitrogen, a Töpler pump removed the hydrogen to a small volume. The estimated error in hydrogen pressure *in the reactor* incurred by this procedure is ±0.1 mm. or $\pm 5 \times 10^{-6}$ mole/liter.

The change of thermal conductivity of the reactant gas was employed in one series of runs as a measure of the amount of hydrogen formed. It was hoped that other reaction products would be similar to diborane in thermal conductance, and so would not interfere with the measurements. Unfortunately this is not so, and it is estimated that these hydrogen values are about 10% low. These data are included in Table IV, but not used in calculations.

Table IV

Rate of Hydrogen Formation in Diborane (Second Slope)

Temp., °C.	Init. B_2H_6 concn., mole/liter × 10²	Rate of hydrogen formation, mole/liter/hour × 10³
110.1	2.101	5.71
	1.270	2.75
	0.425	0.52
100.0	2.541	3.09
	2.148[a]	2.48
	2.146[b]	2.48
	2.145[c]	2.38
	1.670	1.59
	1.331[d]	1.08
	1.288	1.154
	0.887	0.640
90.0	1.156	0.376
80.0	2.825	0.512
	2.296	0.378
	1.721	0.247
	1.151	0.135

[a] Pod. distilled sample from tank A-4. [b] Sample from tank A-1 (undistilled). [c] Sample from tank A-4 (undistilled). [d] Thermal conductivity data.

Materials.—The diborane for reaction was obtained by partial vaporization of small samples stored over liquid nitrogen. Most of these samples had been distilled in a Podbielniak low temperature column from material of tank A-1 containing about 0.05 mole % B_4H_{10} and 0.05 mole % diethyl ether.

One run was made with diborane of tank A-4 containing about 0.5 mole % B_4H_{10} and 0.5 mole % diethyl ether, treated as described in Part II. Small irregularities were observed at the beginning of this run but disappeared after a small interval of time.

Results and Discussion

Inspection of Fig. 3 reveals two rather distinct regions, in each of which there is a characteristic, measurable slope. The "second slope" is more easily dealt with and appears to be related more closely to the other studies reported in this paper. Measured values of this second slope are given in Table IV.

From these values one may calculate the exponent in the expression

$$dC_{H_2}/dt = kc_0^n$$

wherein the derivative refers to the value of the second slope. The resulting numbers are given in Table V for the various temperatures. The agreement leaves little doubt that the correct value is 1.50.

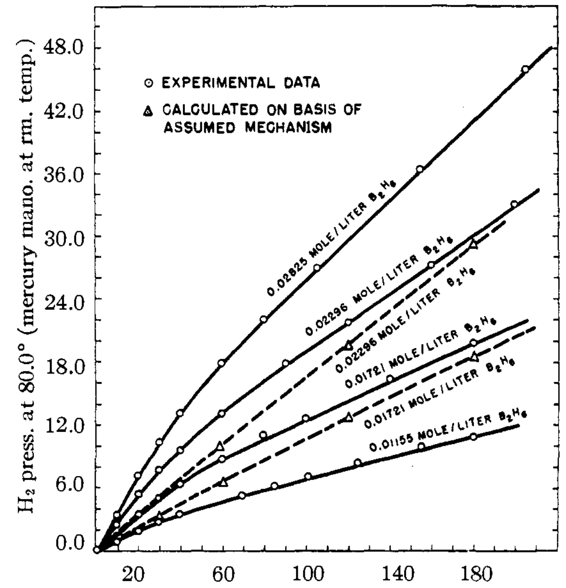

Fig. 3.—Rate of hydrogen formation in B_2H_6 at 80.0°.

TABLE V

THE ORDER OF THE DIBORANE PYROLYSIS FROM THE RATE OF FORMATION OF HYDROGEN

Temp., °C.	Order of the reaction
80.0	1.49
100.0	1.49
110.1	1.50
	1.49 av.

Figure 4 is a plot of the second slope against the 1.5 power of the initial diborane concentration. Straight lines intersecting the origin have been drawn through each set of points, and from their slopes the values of the rate constant given in Table VI are obtained. The activation energy obtained from the temperature dependence of this rate constant is 25.5 ± 0.5 kcal./mole.

TABLE VI

RATE CONSTANTS FOR THE FORMATION OF HYDROGEN IN DIBORANE (SECOND SLOPE)

Temp., °C.	k (liter/mole)$^{0.5}$/hour
80.0	0.109
90.0	0.303
100.0	0.767
110.1	1.888

One may carry through a similar derivation of quantities appropriate to the initial slope of the curves obtained for hydrogen formation in Fig. 3. Table VII contains measured values of this slope, which was unambiguously measurable only at the lower temperatures. Table VIII gives the values of the rate constant obtained from the assumption of 1.5 order, which appears to be valid for this region also. The activation energy obtained is 22.2 ± 0.5 kcal./mole.

TABLE VII

RATE OF HYDROGEN FORMATION IN DIBORANE (FIRST SLOPE)

Temp., °C.	Init. B_2H_6 concn., mole/liter	Rate of hydrogen formation mole/liter/hour
80.0	0.02825	0.000944
	.02296	.000690
	.01721	.000442
	.01151	.000238
90.0	.01156	.000587

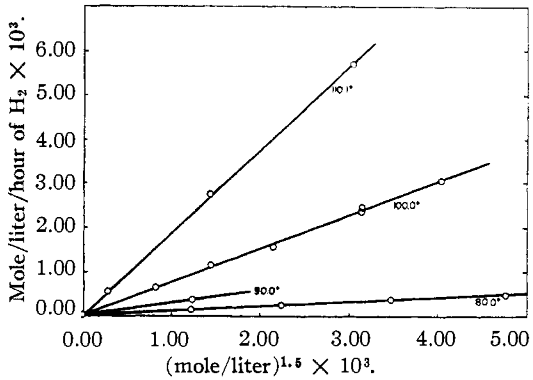

Fig. 4.—Rate of hydrogen formation in B_2H_6 *vs.* initial concn. raised to the 1.5 power.

TABLE VIII

RATE CONSTANTS FOR THE FORMATION OF HYDROGEN IN DIBORANE (FIRST SLOPE)

Temp., °C.	Init. B_2H_6 concn., mole/liter	Rate constant, k (liter/mole)$^{0.5}$/hr.
80.0	0.02825	0.199
	.02296	.198
	.01721	.196
	.01151	.193
		.197 av.
90.0	.01156	.472

IV. Mass Spectrometer Study of Diborane Pyrolysis

Experimental

Apparatus and Operation.—The reaction vessel was a thermostated liter Pyrex bulb. The leak to the mass spectrometer was of 20 mil Fernico sealed to glass, and was prepared by punching a small conical hole in the metal and hammering it nearly shut. This gave a very small leak of quick response.

The pressure in the reaction vessel was of the order of several centimeters, while on the mass spectrometer side it was about 10^{-6} mm. The gas sample for analysis was continuously pumped through the spectrometer; however, since it would require 21 days to reduce the pressure to half-value through the leak, the amount of gas lost in a run of several hours was negligible.

As has been mentioned in part II, experiments with packed reactors indicated that no disturbing catalytic effects were to be expected from the glass walls or the small area of the Fernico leak.

The details and operation of the mass spectrometer have been described.[5] A magnetic scan of the spectrum, at 2000 volts accelerating potential, was made periodically during a run. The scan rate was 15 mass units per minute. From known mass spectra of the pure materials and from previous sensitivity calibrations of the leak, the spectra could be translated into pressure of the constituent hydrides in the reaction vessel.

The characteristic mass peaks used for calibration were

B_2H_6	27
B_4H_{10}	50
B_5H_9	59, 61
B_5H_{11}	59, 61
$B_{10}H_{14}$	117

Figure 5 gives the mass spectra of the first four hydrides. As in all mass spectrometer work, traces of hydrides of

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[5] F. J. Norton, THIS JOURNAL, 71, 3488 (1949).

Table IX

Diborane Pyrolyses

Pressures Interpolated from Plots of Mass Spectrometer Data

Run	Temp., °C.	Initial press., mm.	Mm. of B_2H_6				Mm. of B_5H_{11}				Mm. of B_5H_9			
			t = 1/2 hr.	1	2	3	1/2	1	2	3	1/2	1	2	3
93	120	33.1	29.0	26.5	22.0	17.5	0.72	0.96	0.82	0.64	0.20	0.48	1.04	1.6
259	120	20.8	19.0	17.0	14.3	13.0	0.25	0.25	0.20	0.15	.10	0.22	0.42	0.58
246	110	123.4	120	116	100	84	3.5	4.3	4.0	2.0	.5	1.0	3.5	4.0
235	110	46.9	44	41.5	36.5	32	0.55	0.90	0.93	0.75	.10	.20	0.78	1.2
258	110	22.0	21.5	20.5	18.5	17.0	.22	.33	.38	.33	.02	.06	.21	0.36
255	110	20.7	19.6	19.0	17.8	16.7	.15	.24	.33	.32	.02	.06	.17	.29
91	100	32.5	31.5	31.5	29.5	26.5	.20	.32	.52	.70	.01	.04	.08	.13
Pressures calculated on basis of assumed mechanism														
93	120	33.1	29.7	26.8	22.1	18.6	0.72	0.80	0.70	0.69	0.15	0.40	0.89	1.33
259	120	20.8	19.1	17.6	15.0	13.0	0.37	0.41	0.36	0.33	.07	.21	0.46	0.68
246	110	123.4	113.0	104.3	91.6	83.0	3.06	4.09	4.19	4.00	.31	.95	2.4	3.9
235	110	46.9	44.4	41.8	37.3	35.5	0.78	1.07	1.14	1.06	.08	.24	0.64	1.03
258	110	22.0	21.6	20.5	19.0	17.5	.25	0.36	0.40	0.37	.03	.08	.22	0.35
255	110	20.7	20.0	19.3	17.8	16.6	.23	.33	.36	.34	.02	.07	.20	.32
91	100	32.5	31.7	30.9	29.4	28.3	.25	.41	.57	.62	.01	.04	.13	.24

higher mass than the starting material could be detected and measured in extremely small amounts. The measurement of B_2H_6 in the presence of B_5H_{11}, however, involves subtraction of the contribution of B_5H_{11} to the peak at 27; the precision is not so great in such cases.

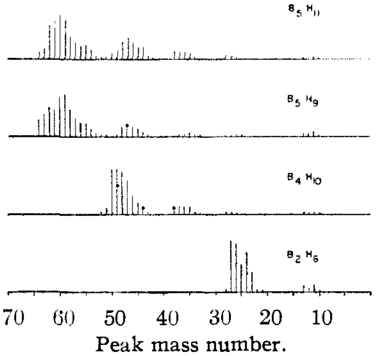

Fig. 5.—Mass spectra of boron hydrides.

Careful calibration for B_5H_9 and B_5H_{11} is necessary since their spectra are so similar. They can readily be distinguished since the ratio of peaks 61 and 59 is 1.05 for pure B_5H_{11} and 0.63 for pure B_5H_9. Calibration with known mixtures of the two shows that this ratio is linearly dependent upon the fractional composition, and is not affected by presence of other hydrides.

In the mass spectrometer studies "sensitivity" is the height of a given mass peak for a given pressure on the leak. For nearly all materials this sensitivity calibration remains constant for hours or days, but in the presence of boron hydrides it may change in a matter of minutes. This is presumably due to changes in emission characteristics of the ion source filament, or contact potential changes. In addition, deposition of non-volatile hydrides on the leak will change the calibration by partially plugging the leak.

All these obstacles were overcome by introducing an internal gas standard. A precisely known amount of argon (from 1 to 2%) was introduced into each reaction or calibrating mixture. The known pressure of argon on the leak gives a standard peak height at mass 40. If changes in its sensitivity occur, there is a proportional change in calibration for the hydrides. This linear relationship can be demonstrated in graphs of "argon sensitivity" *versus* "hydride sensitivity."

Argon has the advantages that its partial pressure on the leak remains constant, and its peak at mass 40 suffers no interference from hydride peaks. Its presence in small amounts was judged to be without significant effect on reaction rates.

Materials.—The diborane used in this work was obtained from the same sources as that of parts II and III. It is possible to prepare very pure B_5H_9 by distillation, and the purity as determined by a cryoscopic method was 99%.[6]

On the other hand, the boron hydrides B_4H_{10} and B_5H_{11} are quite difficult to keep in a pure form because of their rapid decomposition at room temperature. We estimate their purity to be better than 95%.

Results

By this method the thermal decomposition of B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11} and $B_{10}H_{14}$ has been studied. We report here in detail only the experiments with B_2H_6. Only some qualitative features of the other work are needed for the discussion of part V. Detailed reports will be published at a later date.

Figures 6 and 7 are typical of the data obtained, which are represented as points on the graphs of pressure against time. Solid curves represent the theory as presented in part V. The data of 7 runs are summarized in Table IX; the agreement of theory with experiment in Figs. 6 and 7 is typical of all these runs.

Discussion of these results is contained in part V.

V. Discussion

Each of the experiments described in the preceding sections contributes understanding of certain features of the thermal decomposition of diborane. The results of the mass spectrometer are lowest in precision, yet lend themselves most readily to interpretation because of the detail they afford. A simple mechanism will be suggested which is sufficient to account for these observations within experimental error. The more precise results of the pressure studies unfortunately lend themselves less readily to quantitative interpretation because of their sensitivity to the details of an assumed mechanism; nevertheless they serve to suggest certain qualitative elaborations of it.

There are certain general conclusions which may be drawn from the mass spectrometer studies: (1) The non-zero initial rate of formation of B_5H_{11} shows that there are no *time-dependent* intermedi-

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(6) John T. Clarke, Cryogenic Laboratory, The Ohio State University, private communication.

ates involved in its formation. (2) In all the experiments the initial rate of formation of B_5H_{11} was sufficient to account approximately for the entire initial rate of disappearance of B_2H_6. (3) Both the initial concentration and the initial rate of formation of B_5H_9 are zero, which indicates that its partial pressure is an integral of some variable of the reacting system which has the initial value zero.[7] In view of (1) and (2) the natural choice of this variable is the pressure of B_5H_{11}.

There must, of course, be intermediates in the formation of B_5H_{11} from B_2H_6. B_4H_{10}, for example, might be included in the scheme in this way, but on the basis of the mass spectrometer studies there is no justification for doing so. When the predictions of the simple scheme to be postulated are later compared with the experiments on hydrogen formation, however, we will find indication that B_4H_{10} may play an important role as an intermediate.

For the present, we consider the mechanism to be

(a) $B_2H_6 \rightleftarrows 2BH_3$ K

(b) $BH_3 + B_2H_6 \longrightarrow$ Intermediate products $2k_1/5$

(c) Intermediate products $+ B_2H_6 \longrightarrow$
$B_5H_{11} + 2H_2$ rapid

(d) $B_5H_{11} \longrightarrow B_5H_9 + H_2$ k_2

(e) $B_5H_{11} \longrightarrow B_2H_6$, higher hydrides k_3

Steps (a) and (b) are suggested by the 1.5 order observed in the various experiments.

The assumption of step (e) is admittedly crude. Our mass spectrometer studies on thermal decomposition of B_5H_{11} indicate that B_2H_6 is formed at about 2.5 times the rate of formation of B_5H_9, independent of initial pressure and temperature. (These studies will be reported in detail at a later date.) Both B_2H_6 and B_5H_9 appear to be formed in approximately first order reactions from B_5H_{11}, and the activation energy for each process is roughly the same. Because an inaccuracy in the assumption of step (e) (for example, the influence of hydrogen pressure) will have a very small effect on our calculations of the early stages of decomposition of B_2H_6, we have postponed a more detailed investigation of this step. The constant k_3, as determined here, represents the rate of decomposition of B_5H_{11} to products other than B_5H_9, which is individually measured in these experiments. The range of calculation is thus somewhat restricted by the assumption as to order of the B_5H_{11} decomposition in step (e).

While this mechanism is sufficient to account for many of the observed facts, it should be emphasized that there are probably other mechanisms which can do so.

The assumed steps give rise to the rate equations

$$-dx/dt = K^{1/2}k_1x^{3/2} - 2.5k_2y \qquad (1)$$

$$dy/dt = (2/5)K^{1/2}k_1x^{3/2} - (k_2 + k_3)y \qquad (2)$$

$$dz/dt = k_2y \qquad (3)$$

in which $x = P_{B_2H_6}$, $y = P_{B_5H_{11}}$, and $z = P_{B_5H_9}$.

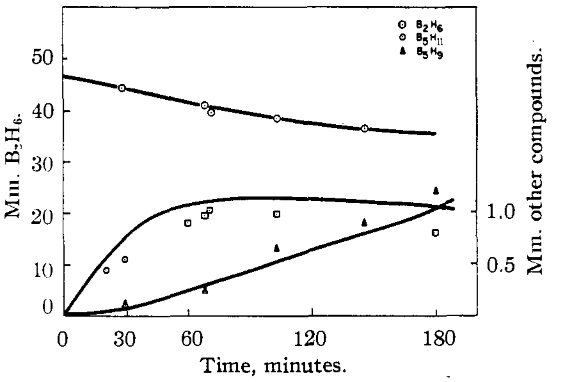

Fig. 6.—Mass spectrograph run no. 235: 46.9 mm. of B_2H_6 at 110°.

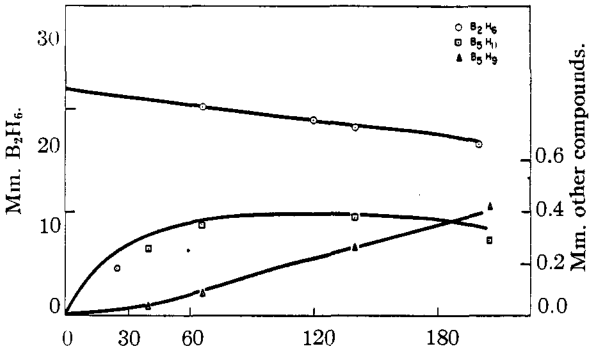

Fig. 7.—Mass spectrograph run no. 258: 22.0 mm. of B_2H_6 at 110°.

With neglect of the term $2.5k_2y$, (1) may be integrated immediately to give

$$x = \frac{4}{Kk_1^2}\left(\frac{1}{t+a}\right)^2 \qquad (4)$$

$$a = 2/(K^{1/2}k_1x_0^{1/2})$$

where x_0 is the initial value of x.

Closed expressions cannot be obtained for y and z, so they must be developed in power series in t. One obtains for $t \ll a$

$$y = P[Q(1 - e^{-(k_2 + k_3)t}) + Rt + St^2] \qquad (5)$$

$$z = k_2P[-(Q/(k_2 + k_3))(1 - e^{-(k_2 + k_3)t}) + Qt + (R/2)t^2 + (S/3)t^3] \qquad (6)$$

wherein

$$P = (2K^{1/2}k_1x_0^{3/2}/5)$$
$$R = -(3/a(k_2 + k_3) + 12/a^2(k_2 + k_3)^2)$$
$$Q = (1/(k_2 + k_3))(R - 1)$$
$$S = 6/a^2(k_2 + k_3)$$

Because of its unimportance as regards the concentrations and times studied by the mass spectrometer, the omitted term in (1) may be included to sufficient approximation by adding to the calculated values of x an amount $2.5z$.

With the constants and activation energies given in Table X, the above equations constitute

TABLE X

RATE CONSTANTS AT 110° AND ACTIVATION ENERGIES

	Value at 110°	Activation energy, kcal./mole
$K^{1/2}k_1$	0.0181 hr.$^{-1}$ × mm.$^{1/2}$	25.5
k_2	0.35 hr.$^{-1}$	18.7
k_3	1.17 hr.$^{-1}$	18.7

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[7] Figures 6 and 7 show that B_5H_{11} occurs very early in the pyrolytic reactions of B_2H_6. Its presence makes very difficult an accurate analysis for B_4H_{10}, the more so as B_5H_{11} increases in concentration. There is some mass spectrometric evidence that a few tenths of a mole per cent. of B_4H_{10} may form very early in the pyrolysis; certainly the amount is never large compared to that of B_5H_{11}.

a reasonably satisfactory account of the observations of the mass spectrometer. Comparisons with these observations are given in Figs. 6 and 7.

Only the activation energy of $K^{1/2}k_1$ can be reasonably precise; the others were determined from mass spectrometer data and suffer from low precision of observations made over a small temperature range.

Hydrogen Formation and Total Pressure

The assumed mechanism gives rise to a dependence of the *initial* rate of hydrogen formation and total pressure rise on the 1.5 power of the concentration. That this relationship persists for rates observed beyond small times is the over-all result of a complicated process involving many individual steps. From the assumed mechanism one can, as detailed below, show in a crude way how this comes about.

With an assumption about the stoichiometry of step (e) of the suggested mechanism, the expected rate of hydrogen formation can be calculated. The over-all production of hydrogen is obtained from the equations

$$\begin{aligned} 5B_2H_6 &\longrightarrow 2B_5H_{11} + 4H_2 \qquad (7)\\ 5B_2H_6 &\longrightarrow 2B_5H_9 + 6H_2\\ 5B_2H_6 &\longrightarrow \text{higher hydrides} + mH_2 \end{aligned}$$

where m is a sort of average number. One obtains

$$P_{H_2} = 2y + 3z + \frac{m}{2}\left(\frac{k_3}{k_2} - 1\right)z \qquad (8)$$

for the pressure of hydrogen at small times. Errors in the assumptions regarding m, or the way in which decomposition of B_5H_{11} to give B_2H_6 occurs, will become important at about one hour at 90°, 30 minutes at 100°, and 15 minutes at 110°.

In a similar way there results for the total pressure at small times

$$P = y/2 + 3z/2 + \frac{(m-4)}{2}\left(\frac{k_3}{k_2} - 1\right)z \qquad (9)$$

Here we have supposed that the higher hydride produced in (7) corresponds on the average to a single gas phase molecule. For this assumption there is only the basis that it gives best agreement with experiment.

A typical comparison of eq. (8) with experiment is made in Fig. 3; here m has been set equal to 6. It will be seen that the predictions are in agreement only asymptotically. In fact, the present scheme cannot possibly show the initial high rate falling off rapidly to an essentially constant value, which is such a striking feature of the hydrogen pressure experiments.

It is important to notice that no such phenomenon is observed in the experiments on total pressure rise. It is this observation which leads us to believe that B_4H_{10} is involved somehow in the early stages of the reaction, since only in the stoichiometry of its formation

$$2B_2H_6 \longrightarrow B_4H_{10} + H_2$$

may one find, among known boron hydrides, a reaction which increases hydrogen pressure but not total pressure.[8]

In connection with the *mechanism* of formation of B_4H_{10} we may observe that, since the *initial* rate of hydrogen formation is approximately 1.5 order, the initial steps are probably the same as in the production of other boron hydrides.

In taking up the work on the total pressure rise, a further remarkable effect must be considered, namely, the apparent discontinuity in the *rate* observed at about one hour of reaction time at 100°. It seems worthwhile to emphasize that this effect occurs at times larger than those at which the hydrogen formation was studied. The assumption we make, illustrated by the stoichiometry of the last step of (7), is that at some time during the reaction a definite change in the nature of this step is induced. This is substantiated by the fact that the rate discontinuity was observed to coincide with the onset of deposition of yellow solids on the walls of the reaction vessel. An increase in the value of m may occur at this point, which would account qualitatively for the increase in the rate of pressure rise. Since this discontinuity occurs when the effects of certain assumptions made here are no longer negligible, we have not investigated this suggestion further.

In Fig. 1 the extent of agreement of eq. (9) with experiment is detailed. In order to obtain even qualitative agreement with $m = 6$ as in the hydrogen pressure work, one must assume the production of an average of 1 gas phase hydride molecule in the last of steps (7).

It must be emphasized that the only significance to be attached to the admittedly crude assumptions regarding this step is that one set of assumptions is consistent with two different sorts of data, taken at various temperatures and various initial pressures of diborane.

SCHENECTADY, N. Y. RECEIVED AUGUST 28, 1950

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[8] It is, however, difficult to see just how this occurs. From mass spectrometer studies in this Laboratory it is known that B_4H_{10} at these temperatures is converted very rapidly to B_5H_{11}. Thus, simply including B_4H_{10} as an intermediate between B_2H_6 and B_5H_{11}, while not incompatible with results of that scheme, does not explain the rapid early change in slope of the hydrogen pressure curves. One must supply also a "brake" which operates to slow down the reaction soon after its inception. Such a "brake" might be due to inhibition by a small amount of B_4H_{10} formed rapidly in the initial stages. That this may actually be the case is indicated by a series of hydrogen pressure runs in which B_4H_{10} was present as an impurity, and in which the initial rapid production of hydrogen was apparently inhibited.