A Preliminary Study of the Kinetics of Pyrolysis of Diborane[1]

BY RICHARD P. CLARKE[2] AND ROBERT N. PEASE

The kinetics of pyrolysis of diborane have been studied between 85 and 163°. The fractional rate appears to be proportional to the square root of the initial pressure (indicating a free radical mechanism) times the 5/2 power of the fraction of diborane unreacted, and is depressed by addition of hydrogen but unaffected by an equivalent amount of nitrogen or by an increase in surface. The reaction is believed to be a radical-type polymerization process complicated by quasi-reversible dehydrogenation.

According to the standard literature,[3] diborane (B_2H_6) undergoes quasi-reversible reactions at room temperature and above producing a series of higher boranes (B_4H_{10}, B_5H_{10}, B_6H_9 and others) with progressive loss of hydrogen. Ultimately (500–700°) the system is converted quantitatively into the elements, which represent the thermodynamically stable state. Although these processes obviously might be described in general terms as a type of condensation polymerization, the details are by no means clear. In particular, the appearance of odd-numbered boranes (e.g., B_5H_9) suggests the intervention of such radicals as borine (BH_3), which would be more characteristic of an addition-chain process. A kinetic study, therefore, seemed to be called for to determine if useful information concerning reaction mechanism could be obtained in this way.

Measurements were carried out at constant volume, the amount of diborane unreacted being determined by fractionation of the gas at the conclusion of each run. The method varied somewhat from series to series but was essentially as follows.

The requisite amount of purified diborane (see below) was let into the reaction bulb at room temperature, and the pressure measured. A large thermostated oil-bath was then brought up around the reaction bulb. After a suitable time-interval the bath was lowered, the bulb was quickly wiped and washed with acetone after which it was chilled in liquid nitrogen. It was next brought back to room temperature, and a final pressure was read. This procedure involves uncertainties in starting and stopping times, though it is true that effects on heating and cooling partially compensate one another. Sintered-glass mercury cut-offs or break-off seals were employed wherever possible to avoid exposure to stopcock grease.

Hydrogen was determined by pumping at liquid nitrogen temperature, and reading the residual pressure at room temperature. The unreacted diborane was next removed at −138° (m.p. of n-bu-

tane), where the normal vapor pressure of diborane is about 25 mm., and the residual pressure at room temperature measured. From these data, the initial pressure at reaction temperature, the fraction of diborane remaining, the ratio of hydrogen formed to diborane reacted, and the pressure of higher boranes volatile at room temperature could be calculated.

Several types of reaction bulbs were used—one of silica, others of Pyrex, some initially clean, some coated with reaction products and one filled with Pyrex wool—but in no case was any pronounced surface activity apparent.

Diborane was purified by pumping at liquid nitrogen temperature to remove hydrogen, and subsequently distilling from a bath of melting n-butane (m.p. −138°).[4]

Series of runs at 103.4° and initial pressures of about 50, 100 and 200 mm. (Table I) led to the following conclusions: (1) First order, three-halves order, and second order "constants" all fall as the fraction converted increases. (2) For equal fractional conversions, the three-halves order "constants" are more nearly independent of initial pressure. (3) Hydrogen in the initial ratio 1.5 $H_2/1$ B_2H_6 decreases the rate very considerably, whereas equal amounts of nitrogen are without effect. (4) A packing of Pyrex wool does not markedly alter the rate.

A considerable amount of time was given to obtaining a satisfactory rate equation. There was more than a suspicion that quasi-reversibility was responsible for the falling constants, especially in view of the depressant effect of added hydrogen. However, when particular mechanisms were invoked it soon became apparent that a combination of experimental error and the large number of adjustable constants rendered such analyses meaningless. It was subsequently found that the relatively simple rate equation

$$-dx/dt = k' p_0^{1/2} x^{5/2}$$

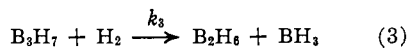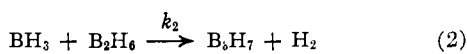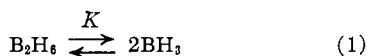$$k' = \frac{2}{3 p_0^{1/2} t}(x^{-3/2} - 1)$$

gave reasonably consistent constants for most series. Such constants appear in the last column of Tables I and II. (The latter table presents data at other temperatures.) This relation preserves the observed dependence on initial pressure, p_0, and affords the required higher-power dependence on fraction, x, unreacted. Further trials revealed that the rate equation is consistent with the mechanism

$$B_2H_6 \underset{K}{\rightleftarrows} 2BH_3 \quad (1)$$

$$BH_3 + B_2H_6 \xrightarrow{k_2} B_3H_7 + H_2 \quad (2)$$

$$B_3H_7 + H_2 \xrightarrow{k_3} B_2H_6 + BH_3 \quad (3)$$

$$B_3H_7 + B_2H_6 \xrightarrow{k_4} B_4H_{10} + BH_3 \quad (4)$$

the net reaction being

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

Actually, the amount of B_4H_{10} and other volatile higher boranes recovered (residual pressure after separation of hydrogen and diborane) was but a small fraction of that required by the above reaction; and the ratio of hydrogen recovered to diborane reacted was not $1/2$ as required but ranged from a little less than 1 in the early stages toward 2 as the reaction approached completion. This is entirely consistent with earlier work[3] which reveals

TABLE I

PYROLYSIS OF DIBORANE AT 103.4°

p_0, init. press. B_2H_6, mm.
p_0', init. press. H_2 or N_2, mm.
t, time, sec.
x, fractn. B_2H_6 unchanged
k_1, first order constant
$k_{3/2}$, three-halves order const.
k_2, second order constant
k', exptl. const. (see text)

p_0	p_0'	t	x	$k_1 \times 10^5$	$k_{3/2} \times 10^6$	$k_2 \times 10^7$	$k' \times 10^6$
48.2	...	3600	0.935	1.9	2.8	4.0	2.8
48.4		14400	.824	1.4	2.0	3.0	2.2
48.7		28800	.675	1.4	2.2	3.4	2.7
44.8		43200	.602	1.2	2.0	3.4	2.6
49.3		144000	.331	0.8	1.5	2.9	2.8
102.9		3600	.905	2.8	2.8	2.8	3.0
99.7		7200	.851	2.2	2.3	2.4	2.5
103.2		33480	.540	1.8	2.1	2.5	3.0
104.5		45600	.451	1.8	2.1	2.6	3.3
103.9		86400	.359	1.2	1.5	2.0	2.8

Nitrogen added initially

100.8	165.0	7200	0.836	2.5	2.6	2.2	2.9
106.2	153.1	14400	.700	2.5	2.7	2.8	3.2
97.7	207.2	57600	.403	1.6	2.0	2.6	3.4
98.5	125.0	129600	.307	0.9	1.3	1.8	2.4

Hydrogen added initially

101.3	159.4	3600	0.945	1.6	1.6	1.6	1.6[a]
101.5	150.2	7200	.916	1.2	1.3	1.3	1.3
101.3	152.6	14400	.886	0.8	0.9	0.9	0.9
101.3	163.7	36000	.803	.6	.6	.7	.7
100.8	155.1	79200	.673	.5	.6	.6	.7
200.0	...	3600	.878	3.6	2.5	1.8	2.8
		7200	.812	2.9	2.2	1.6	2.4
		14530	.691	2.5	2.0	1.5	2.4
		28800	.556	2.0	1.7	1.4	2.3
		50400	.437	1.6	1.4	1.3	2.3
		86400	.363	1.2	1.1	1.0	1.9

Reaction vessel packed with Pyrex wool

199.3		14400	0.696	2.5	2.0	1.5	2.4
201.7		36000	.462	2.1	1.8	1.6	2.8
200.3		129900	.221	1.2	1.2	1.4	3.1

[a] Values of k' with added hydrogen have been calculated without allowing for the addition in order to emphasize that rates are in fact lowered.

TABLE II

PYROLYSIS OF DIBORANE AT VARIOUS TEMPERATURES

p_0	p_0'	t	x	k'
		Temp. 85.0°		
57.7	..	1800	0.995	....
		7200	.970	5.7 × 10⁻⁷
162.4		3600	.975	5.7
		7200	.957	4.9
		14400	.900	6.2
179.7		3600	.973	5.8 × 10⁻⁷
		7200	.955	5.0
		14400	.924	4.4
		21600	.895	4.2
		Temp. 121.8°		
63.6		3600	0.761	1.2 × 10⁻⁶
		6200	.681	1.1
		14400	.468	1.2
107.3		3600	.732	1.1 × 10⁻⁵
		7200	.560	1.2
		14400	.413	1.2
		28800	.296	1.2
148.1		1800	.810	1.1 × 10⁻⁵
		3840	.689	1.1
		6200	.571	1.2
		14400	.405	1.1
		Temp. 140.0–140.5°		
29.3		600	0.803	8.0 × 10⁻⁵
29.1		1200	.693	7.5
29.3		1990	.620	6.5
30.2		6540	.306	9.1
35.6		970	.733	6.8
36.2		2000	.574	7.2
35.6		4510	.380	8.1
		Temp. 162.5–164.5°		
23.9		210	0.750	3.6 × 10⁻⁴
24.1		330	.678	3.3
22.3		500	.601	3.2
24.6		680	.497	3.7
23.7		990	.386	4.4
24.2		1400	.277	5.7
23.7		1900	.221	6.2
37.3		190	.753	3.1 × 10⁻⁴
37.1		340	.643	3.1
36.6		670	.435	4.1
37.3		1180	.288	5.1
38.6		1660	.223	5.5
38.3		2450	.171	5.8
37.6		3640	.120	6.9
37.3		6000	.078	8.2
		Hydrogen added initially		
39.8	99.3	680	0.578	2.0 × 10⁻⁴[a]
35.4	88.4	1290	.514	1.5
36.9	88.6	3980	.232	2.2
36.8	98.7	43200	.016	...

[a] See note at end of Table I.

the presence of less volatile higher boranes (e.g., $B_{10}H_{14}$) and ultimately elementary boron and hydrogen, for which the ratio of hydrogen formed/diborane reacted would be 3. A more serious shortcoming of the above mechanism is its neglect of quasi-reversibility in the later stages which certainly is present since the first preparation of diborane was effected by the pyrolysis of the tetraborane, B_4H_{10}.

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

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

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 $E_2 + \frac{1}{2}\Delta H_1^0$. 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.
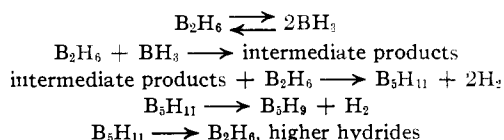

Kinetics of Pyrolysis of Diborane[1]

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

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

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

(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.

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