Thermal Decomposition of Diborane. Part I. The Decomposition Mechanism at Low Conversion and Temperature and the Inhibiting Effect of Accumulated Hydrogen

By **Héctor Fernández, Juan Grotewold,*** and **Carlos M. Previtali,** Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Buenos Aires, Argentina

A gas recirculating device was used to trap the condensible products at −130 °C at the exit of the reaction vessel. The reaction order was three halves in diborane concentration. The Arrhenius parameters, admittedly low, are: $\log A/(\mathrm{cm}^{3/2}\ \mathrm{mol}^{-1/2}\ \mathrm{s}^{-1}) = 4{\cdot}72 \pm 0{\cdot}14$ and $E_a = 42{\cdot}47 \pm 1{\cdot}17$ kJ mol^{-1}. The reaction, however, is considered to be truly homogeneous since neither coating nor changes in surface:volume ratio altered the rate constant found in an aged reaction vessel. The decomposition was also studied in a static system. For reaction times shorter than 200 s a marked decrease of the rate constant with time was observed. After this interval the rate constant stabilizes and remains almost constant and the figures found are similar to those reported in previous studies. A competitive reaction between an intermediate and hydrogen (inhibition) or diborane is suggested to account for the initial decrease of the rate constant. The decomposition of products (principally B_5H_{11}) is held responsible for the observed constancy of the rate constants after the first 10 min of reaction.

SINCE diborane is the smallest stable boron hydride molecule and seems to play an important role in the preparation and decomposition of larger hydrides, an understanding of its thermal decomposition would be useful.[1-5] The generally accepted mechanism [1-5] is reactions (1)—(3), with the decomposition of B_3H_9 as the rate-determining step.[4] The order of the reaction is $\frac{3}{2}$ and the experimental activation energy for diborane decomposition is *ca.* 27 kcal mol^{-1}.[5] Although this scheme suggests a simple mechanism, several facts suggest a greater complexity. If hydrogen formation is followed, the rate appears faster and the activation energy seems considerably smaller (22 kcal mol^{-1}) than when diborane decomposition is measured.[2]

$$B_2H_6 \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} 2BH_3 \qquad (1)$$

$$BH_3 + B_2H_6 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B_3H_9 \qquad (2)$$

$$B_3H_9 \xrightarrow{k_3} B_3H_7 + H_2 \qquad (3)$$

Hydrogen inhibits the decomposition of diborane. Clarke and Pease [1] attempted a kinetic study of this effect but it can by no means be considered conclusive. Even the stoicheiometry of the reaction is not well defined (B_5H_{11}, B_5H_9, B_4H_{10}, and $B_{10}H_{14}$ are very often major borane products depending on the extent of pyrolysis) and it seems that further decomposition of the products may be kinetically important since it is known that some products catalyse the decomposition of diborane.[6] Since previous work was done in static reaction vessels the presence of considerable amounts of these products was unavoidable.

Therefore, in order to remove higher boron hydrides from the reaction mixture a gas recycling system was used and the gases which are less volatile than diborane were trapped at the outlet of the reaction vessel.

EXPERIMENTAL

The device used to obtain a continuous diborane flow through the reaction vessel was a glass tube (30 cm long; 30 mm i.d.) tightly fitted to a plastic piston containing a magnetic iron rod coated with epoxy resin. The displacement was produced by the movement of an external permanent magnet driven by an electric motor. Four different glass valves ensured a continous gas flow. Although the flow rate was not measured, a four-fold change in the speed of the piston did not affect the decomposition

---

[1] R. P. Clarke and R. N. Pease, *J. Amer. Chem. Soc.*, 1951, **73**, 2132.

[2] J. K. Bragg, L. V. McCarty, and F. J. Norton, *J. Amer. Chem. Soc.*, 1951, **73**, 2134.

[3] K. Borer, A. B. Littlewood, and C. S. G. Phillips, *J. Inorg. Nuclear Chem.*, 1960, **15**, 316.

[4] R. E. Enrione and R. Schaeffer, *J. Inorg. Nuclear Chem.* 1961, **18**, 103.

[5] L. H. Long, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1097.

[6] J. A. Dupont and R. Schaeffer, *J. Inorg. Nuclear Chem.*, 1960, **15**, 310.

rate. A cylindrical reaction vessel was used (53·1 cm^3; $s/v = 1{\cdot}8$) but in some runs it was replaced by a helical capillary tube (4 mm i.d.) to achieve a higher surface : volume ratio (12·7 cm^3; $s/v = 10$). Pumping rates were considerably smaller for this system. Diborane was preheated by passage through a capillary tube (10 cm long; i.d. 4 mm) at the inlet of the reaction vessel. At the outlet of the cell the gas mixture entered a trap at −120 to −130 °C where all compounds except diborane and hydrogen were condensed. The temperature of the trap set a higher limit to the diborane pressure which could be used. A second trap completed the recycling device. The second trap could be isolated from the rest of the system by two greaseless Springham stopcocks. It was also fitted with a mercury manometer. Runs were started by opening the two greaseless stopcocks and allowing a previously measured amount of diborane to expand. The ratio between the volume of the total system and the volume between stopcocks had been previously determined with CO_2 under similar conditions. The cell was immersed in water- or oil-baths and the temperature was kept constant within 0·5 °C. The reaction was ended by cooling the second trap with liquid nitrogen and freezing all substances except hydrogen. This was the only product measured and it was done with a Toeppler pump.

TABLE 1

Rate of diborane decomposition by the recirculating technique

No.	$t/°$ C	Time/s	$10^7[B_2H_6]$ / mol cm^{-3}	$10^{12}R_{H_2}$ / mol cm^{-3} s^{-1}	10^2k / cm$^{3/2}$ mol$^{-1/2}$ s^{-1}
38a	69·5	3600	8·51	4·42	0·56
34a	70·2	3600	6·73	3·24	0·61
35a	70·2	3600	6·73	3·40	0·62
120b	70·5	3600	5·30	2·30	0·60
36a	90·0	3600	7·24	8·21	1·40
37a	90·0	3600	7·96	9·52	1·35
77b	90·0	1800	7·60	9·32	1·44
5a	92·0	3600	7·66	10·34	1·54
6a	92·0	3600	4·33	4·42	1·55
11a	92·0	1800	10·33	13·74	1·30
13a	92·0	1800	6·96	8·06	1·39
17a, e	92·0	1800	5·82	6·16	1·39
19a, e	92·0	1800	5·25	5·37	1·41
20a, e	92·0	3600	5·18	5·45	1·46
22a	92·0	3600	3·51	3·23	1·55
106f	92·0	3600	7·54	8·89	1·36
107f	92·0	3600	7·03	8·54	1·39
Average of 23 determinations at 92 °C: 1·43 ± 0·07					
33a	100·0	3600	7·38	14·37	2·27
39a	110·0	1800	5·57	12·48	2·99
67b	110·0	3600	6·60	13·43	2·51
72b	110·0	1200	6·52	14·45	2·74
73b	110·0	5400	6·52	14·37	2·73
Average of 9 determinations at 110 °C: 2·73 ± 0·18					
28–1a	112·0	900	5·98	13·27	2·87
28–2a	112·0	1800	5·96	13·11	2·85
28–3a	112·0	7200	5·93	13·11	2·87
28–4a	112·0	300	5·79	12·79	2·90
28–5a	112·0	1800	5·78	12·79	2·91
74–b	121·0	1800	6·14	20·06	4·17
112c	121·0	1800	5·40	16·40	4·05
113c	121·0	1800	3·95	9·99	4·10
114–1b	121·0	1800	6·08	19·00	3·98
114–2b	121·0	7200	6·08	16·20	3·38
114–3d	121·0	1800	6·08	27·60	5·70
117–1b	121·0	1800	6·20	19·70	4·02
117–2b	121·0	10800	6·20	15·20	3·10
117–3d	121·0	1800	6·20	35·00	7·10
30–1a	131·0	3600	7·59	67·00	10·14
30–2a	131·0	3600	7·38	65·80	10·38
30–3a	131·0	1800	7·16	66·60	11·01
30–4a	131·0	900	7·06	71·30	12·02
30–5a	131·0	300	7·00	83·20	14·21
30–6a	131·0	300	6·98	82·30	14·11
30–7a	131·0	1800	6·96	64·20	11·06
30–8a	131·0	900	6·86	69·40	12·21
30–9a	131·0	3600	6·80	61·10	10·71

a, Aged vessel; b, vessel covered with Teflon; c, four-fold change in flow rate; d, accumulated B_5H_{11} released into the system without use of the cold trap; e, added CO_2; Run 17: 68 Torr; Run 19: 92 Torr; and Run 20: 339 Torr; f, capillary vessel.

Diborane was prepared according to Norman and Jolly,[7] purified by several trap-to-trap distillations, thoroughly degassed, and kept under liquid nitrogen. The static system consisted of a cylindrical reaction vessel (52·1 cm^3; $s/v = 1{\cdot}8$) connected through capillaries to a mercury manometer and to a high-vacuum glass stopcock. In subsequent runs the reaction vessel was filled with

---

[7] A. D. Norman and W. L. Jolly, *Inorg. Synth*, **1968**, **11**, 15.

glass tubes and coated with Teflon (45·0 cm³; s/v = 41·4). The reaction was started by opening quickly the stopcock to a volume filled with diborane, but in some runs a cold finger, where diborane had been previously stored and degassed, was rapidly warmed. The reaction was ended by opening the stopcock so that the gas expanded through a trap with liquid nitrogen to a large volume. The hydrogen formed was then pumped off and measured in a Toeppler pump.

RESULTS AND DISCUSSION

Recycling Technique.—Results between 69·5 and 131·0 °C are in Table 1. The reaction order is three-halves in diborane concentration. It increases markedly above 150 °C (see Figure 1). These results are in qualitative agreement with previous work.[2]

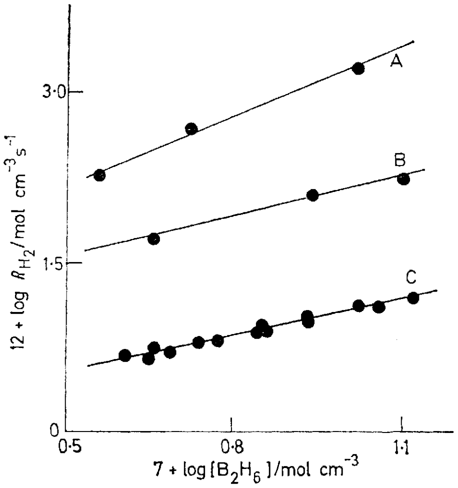

FIGURE 1 Plot of log R_{H_2} against the log [B_2H_6] at (recirculating technique) A, 177 °C; B, 145 °C; and C, 92° C

In order to be able to measure the decrease of the reactants, in some runs (27—29) the diborane that had not reacted was used again, up to 15 times, before its concentration was measured (see Table 2). The ratios of the total amount of hydrogen formed to the amount of diborane decomposed are at 112 °C: 0·8 ± 0·2; 0·64 ± 0·2; and 0·9 ± 0·1 respectively, which corresponds, within experimental error, to stoicheiometry $\frac{5}{2}B_2H_6 \longrightarrow B_5H_{11} + 2H_2$. At 148 °C this ratio had increased to 1·49.

TABLE 2

Ratio of total amount of hydrogen formed to diborane decomposed at different temperatures

No.	t/° C	$10^7[B_2H_6]_i$ / mol cm^{-3}	$10^7[B_2H_6]_f$ / mol cm^{-3}	$10^7\Sigma[H_2]$ / mol cm^{-3}	$\Sigma[H_2]$ / $\Delta[B_2H_6]$
27	112·0	6·90	6·66	0·192	0·80
28	112·0	5·98	5·78	0·130	0·65
29	112·0	5·71	5·13	0·522	0·90
30	131·0	7·59	6·80	1·193	1·51
24	148·0	7·47	5·50	2·797	1·42
25	148·0	7·80	5·82	3·088	1·56
26	148·0	5·26	3·99	1·892	1·49

The results are independent of added inert gases, reaction times, and flow rates. Figure 2 shows the plot of the logarithm of the rate constant for hydrogen formation against the inverse of temperature. Each point is the average of several determinations. The Arrhenius parameters corresponding to the linear part of the curve at low temperatures are: log A/(cm$^{3/2}$ mol$^{-1/2}$ s^{-1}) = 4·22 ± 0·14 and E_a = 10·16 ± 0·28 kcal mol^{-1}.

The disagreement with previous results is obvious.[2] Since large rate constants, especially at low temperatures, considerably lower activation energies, and small A factors are very often associated with a heterogeneous reaction, it is convenient to discuss the arguments favouring a truly homogeneous process. When a clean, well degassed Pyrex vessel was used, it was definitely necessary to age it. The process was slow and it was sometimes several weeks until reproducible results could be obtained. This was particularly bad after an unwanted oxidation of diborane in the reaction vessel had occurred. Since ageing alone does not ensure the absence of heterogeneity the cell was covered with Teflon by polymerization of C_2F_4 with di-t-butyl peroxide at 160 °C.[8] Similar results were obtained.

Since it is not allowable in a circulating system to fill the cell with glass tubes the s/v ratio was increased by a factor of five by using a 4 mm i.d. capillary tube also coated with Teflon. Again no difference in rate constants was observed. Therefore a heterogeneous reaction seemed unlikely.

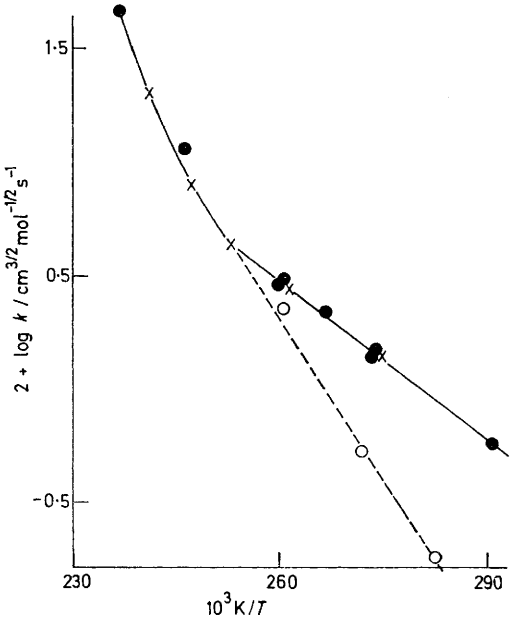

FIGURE 2 Plot of log k against the inverse of temperature: Recirculating technique: ●, aged vessel; ×, vessel coated with Teflon; ○, static system

Static System.—The pyrolysis of diborane in a static system was studied to seek an explanation of the disagreements between previous work and our results with the recycling technique. Since the measurement

---

[8] R. Solly, D. M. Golden, and S. Benson, *Internat. J. Chem. Kinetics*, 1970, **2**, 381.

of hydrogen formation is far more sensitive than pressure measurement, we chose it. For reaction times longer than 10 min agreement with Bragg *et al.*[2] was obtained. The same values of rate constants and energy of activation (23 kcal mol^{-1}) were determined (Figure 2). Comparison with results from the recycling technique revealed that one of the main differences between both methods may be the considerably larger concentration of products formed in the static system. Small diborane pressures and a large dead space in the recycling system contributed to make this possible.

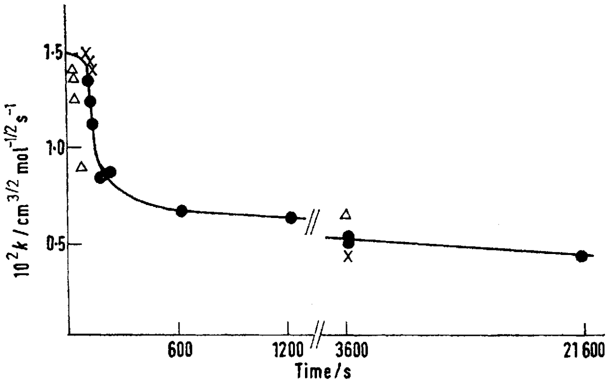

FIGURE 3 Plot of k against time in the static system. ● 50 Torr < $p(B_2H_6)$ < 300 Torr; △ $p(B_2H_6)$ > 300 Torr; × $p(B_2H_6)$ < 50 Torr

Therefore, in the static system, an increase of the experimental rate constant $k_{exp} = R_{H_2}[B_2H_6]^{-3/2}$ for short reaction times should be observed, as confirmed by Figure 3. Neither coating with Teflon nor filling the reaction vessel with glass tubes (also coated) increasing s/v by a factor of 23 altered the results. This excludes almost completely the possibility of an initial heterogeneous decomposition followed by a fast ageing of the reaction vessel. Results are in Table 3. In order to test whether the presence of B_5H_{11} was necessary to observe inhibition or if the mere accumulation of hydrogen could account for it, runs with long reaction times were performed at 121·0 °C by use of the recirculating technique (runs 114-2b and 117-2b of Table 1). Although at 121 °C inhibition is less marked, this temperature was chosen to avoid too long reaction times. It was observed that hydrogen alone suffices to account at least in part for the observed inhibition. However, once hydrogen had been pumped off, the cold trap, where all the B_5H_{11} had been collected, was warmed, and half-hour runs (without cold trap) performed. The results leave no doubt about a marked increase in the rate of hydrogen formation. Therefore even at low concentrations the accumulation of products in the reaction vessels is important in the rate of hydrogen formation (runs 114-3d and 117-3d of Table 1). We suspect that this might be the reason for the change in the mechanism observed at low reaction times in the static system.

TABLE 3

Rate of diborane decomposition using a static system

No.	t/°C	Time/s	$10^6[B_2H_6]$ mol cm^{-3}	$10^{10}R_{H_2}$ mol cm^{-3}	10^2k cm$^{3/2}$ mol$^{-1/2}$ s^{-1}
91a	80·0	21 600	11·00	0·50	0·13
101b	90·9	159	7·78	1·73	0·81
97a	92·0	3 600	8·14	1·06	0·50
98a	92·0	21 600	9·28	1·01	0·44
99a	92·0	185	8·92	2·25	0·84
100a	92·0	127	8·59	2·85	1·13
102b	92·0	197	6·68	1·53	0·88
103b	92·0	200	5·62	1·14	0·85
104b	92·0	3 600	5·84	0·67	0·53
105b	92·0	112	4·74	1·27	1·23
108b	92·0	101	4·90	1·45	1·35
109b	92·0	100	22·00	8·80	0·90
110b	92·0	615	4·20	0·57	0·67
111b	92·0	1 200	4·20	0·52	0·64
121b	92·0	132	2·12	0·45	1·40
122b	92·0	120	1·98	0·41	1·46
123b	92·0	112	2·21	0·51	1·48
124b	92·0	25	33·40	23·70	1·26
125b	92·0	31	13·30	6·60	1·40
126b	92·0	30	13·10	6·50	1·44
128b	92·0	3 600	33·40	10·80	0·63
129b	92·0	3 600	0·88	0·036	0·47
92a	95·0	21 600	10·00	1·18	0·40
93a	110·0	5 400	11·30	7·05	1·80
94a	110·0	315	10·30	7·07	2·14
95a	110·0	5 400	9·64	5·50	1·79
96a	130·0	3 840	8·56	18·80	7·50

a, Vessel A: 52·1 cm^3; s/v: 1·8. b, Vessel B: 45·0 cm^3; s/v: 41·4.

Since the assumption that hydrogen inhibition arises from a competitive reaction between an intermediate with hydrogen or diborane seemed reasonable, rate equation (4) was tested. Here k_{ni} stands for the un-

$$R_{H_2} = \frac{k_{ni}\,.\,[B_2H_6]^{3/2}}{1 + k'\,.\,[H_2]/[B_2H_6]} \tag{4}$$

inhibited rate of hydrogen formation (*i.e.*, the rate constants measured with recycling technique). If the concentration of diborane remains approximately constant during a run (low conversions), then equation (4) can easily be integrated, leading, after some rearrangement, to equation (5). Therefore a plot of

$$\frac{k_{ni}\,.\,[B_2H_6]^{3/2}\,.\,t}{[H_2]} = \frac{k'}{2}\cdot\frac{[H_2]}{[B_2H_6]} + 1 \tag{5}$$

the left-hand side of equation (5) against $[H_2]/[B_2H_6]$ should give a straight line with a value of unity for the intercept. This was done in Figure 4.

Since we suspect that the change in mechanism observed in Figure 3 at short reaction times (less than 4 min) in the static system is produced by further decomposition of reaction products, only runs with very low conversions were taken into account. Thus significant decomposition was avoided. The agreement is, in view of the experimental difficulties, surprisingly good.

Any mechanism suggested to explain the thermal decomposition of diborane at short reaction times will therefore have to allow for the existence, after the rate-determining step, of a competing reaction between an unknown intermediate with hydrogen (inhibition) or with diborane.

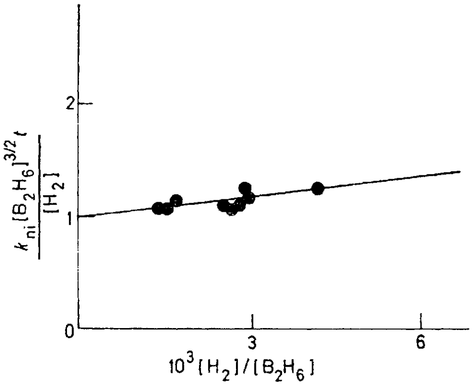

FIGURE 4 Plots for short periods in the static system (see text)

Several mechanisms, in qualitative agreement with these experimental facts, have been suggested.[1,5] All of them fail to give satisfactory agreement between the low experimental A factor and the one estimated for each mechanism. However the mechanism shown in reactions (6)—(10) seems to fit better with the experimental data than any of the others for short reaction times. Steps 1, −1, 2, −2, and 3 correspond

$$2B_2H_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BH_3 + B_3H_9 \qquad (6)$$

$$BH_3 + B_2H_6 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B_3H_9 \qquad (7)$$

$$B_3H_9 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} B_3H_7 + H_2 \qquad (8)$$

$$B_3H_7 + B_2H_6 \xrightarrow{k_4} B_4H_{10} + BH_2 \qquad (9)$$

$$BH_3 + B_4H_{10} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} B_5H_{11} + H_2 \qquad (10)$$

to the hydrogen-uninhibited reaction, where step 3 (the decomposition of B_3H_9) is rate determining. Steps 1 and −1 have recently been suggested by Long [5] who attempted to rationalize the decomposition of boron hydrides. Although steps 1, −1, 2, and −2 cannot be distinguished thermodynamically from reactions (11)

$$B_2H_6 \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} 2BH_3 \qquad (11)$$

$$2\,.\,(BH_3 + B_2H_6 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B_3H_9) \qquad (12)$$

and (12) since both correspond to the overall reaction (13), step 1 seems more likely from purely kinetic

$$3B_2H_6 \rightleftharpoons 2B_3H_9$$

considerations. It is well known that isotopic mixing between B_2H_6 and B_2D_6 occurs readily at room temperature.[4] There is no apparent reason to believe that the mechanism should differ from the initial reactions suggested for the decomposition of diborane (steps 1 and 2). However even the lowest figure for the bond-dissociation energy of diborane, 34—35 kcal mol^{-1},[9] would make a fast equilibrium between diborane and borine at that temperature almost impossible. Steps 4, 5, and −5, were included in the mechanism because it is generally accepted that there is a fast equilibrium between B_4H_{10} and B_5H_{11} and it has been suggested that B_5H_{11} is produced by B_4H_{10}.[5] However from the results of this work they cannot be distinguished from reaction (14), since the initial stoicheiometry found here

$$B_3H_7 - B_2H_6 \xrightarrow{k_6} B_5H_{11} + H_2 \qquad (14)$$

corresponds to (15). By use of the steady-state hypo-

$$\tfrac{5}{2}B_2H_6 \longrightarrow B_5H_{11} + 2H_2 \qquad (15)$$

thesis for the unhibited reaction, the rate of formation of hydrogen is given by equation (16) where K_1 and K_2

$$R_{H_2} = 2k_3K_1^{\frac{1}{2}}K_2^{\frac{1}{2}}[B_2H_6]^{3/2} = k_{ni}[B_2H_6]^{3/2} \qquad (16)$$

are the equilibrium constants of steps 1 and 2 respectively.

To obtain equation (16) equation (17) had to be assumed, and that $k_3 \ll k_{-2}$. Both assumptions seem to

$$\frac{K_2}{K_1} \cdot \frac{k_3}{k_{-1}} \ll 16\ (B_2H_6) \qquad (17)$$

be reasonable if step 3 is rate-determining.

To derive equation (4) it has been supposed that step 3 is slow compared with steps −2 and −1 so that the stationary concentration of B_3H_9 will not be substantially altered with respect to the non-inhibited reaction. A rigorous treatment leads to the same results as long as it is accepted that $k_{-3} \ll k_{-2}$ or k_{-1}. According to the mechanism k' in equation (4) stands for k_{-3}/k_4. In order to estimate the A factor corresponding to k_{ni}, the entropies for B_2H_6 and B_3H_9 were taken as 55·7 and 58·0 cal mol^{-1} K^{-1} respectively (standard state 1 atm). The loss of a hydrogen molecule by B_3H_9 necessarily involves at least one additional three-membered ring in the activated state. Therefore the activation entropy of step 3 might be small. An A factor of 10^{10} s^{-1} for k_3 should be taken as a lower limit.

Even so, use of a standard state 1 mol l^{-1} leads to the calculated A factor given in equation (18) which is

$$A_{calc} = A_3 \exp(\Delta S_1/2R) \exp(\Delta S_2/2R) = 10^{10} \times 10^{-42\cdot8/9\cdot2} = 10^{5\cdot2}\ l^{\frac{1}{2}}\ mol^{\frac{1}{2}}\ s^{-1} \qquad (18)$$

still over two magnitude orders higher than the experimental A factor of $10^{2\cdot72}$ l$^{\frac{1}{2}}$ mol$^{\frac{1}{2}}$ s^{-1}. Several other possible mechanism were examined but the agreement between those mechanisms of three-halves order and experimental results were even less satisfactory.

Since the most obvious source of this discrepancy is the possible existence of a heterogeneous reaction the system was thoroughly tested for it. Although no one of the procedures, ageing of the reaction vessel, changes in surface : volume ratios, coating of the reaction vessel, or the addition of inert gases suffices by

---

[9] (*a*) M. E. Garabedian and S. Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 176; (*b*) A. B. Burg and Y. Chinfu, *ibid.*, 1966, **88**, 1147; (*c*) J. Grotewold, E. Lissi, and A. E. Villa, *J. Chem. Soc.* (*A*), 1966, 1038.

itself to rule out the participation of a heterogeneous reaction, the failure of all of them to reveal it makes its existence highly improbable. Moreover the fact that the rate constants obtained from the static system seem to extrapolate at short reaction times to the figure found with the recycling device is good evidence for a truly homogeneous reaction. Therefore the differences in the A factor could be due either to a wrong estimate of the elementary rate constants or to an incorrect mechanism. The latter possibility seems to be the most likely.

Mechanism of Diborane Pyrolysis for Long Reaction Times in the Static System.—Figure 3 shows that after a few minutes of pyrolysis a clear change in the decomposition mechanism occurs. The reaction time at which this is achieved depends on the initial diborane pressure, being shorter for larger amounts of reactants. Almost all previous work had been done under these conditions. For reaction times longer than 1000 s the rate expression: $R_{H_2} = k_{exp}[B_2H_6]^{3/2}$ had to be integrated to account for the change in diborane concentration with time. The stoicheiometry of the reaction was supposed to be $\frac{5}{2}B_2H_6 \longrightarrow B_5H_9 + 3H_2$. Figure 3 shows that the rate constant decreases slowly with time. It was also observed that for constant reaction times (3600 s) the rate constant increases with increasing diborane pressure. The same trend can be observed in the work of Clarke and Pease.[1] It therefore seems reasonable to suppose that the observed change in mechanism is the result of a subsequent decomposition of B_5H_{11} and although the simple mechanism given earlier and accepted so far for this reaction [reactions (1)—(3)] fits the experimental data adequately, it cannot be true. There is substantial evidence for a fast decomposition of B_5H_{11}. According to the literature this occurs readily at room temperature [10] and there is clear evidence in this work that at 121 °C the rate of hydrogen formation increases markedly when, even in relative low concentrations, B_5H_{11} is added to diborane. Therefore, the fact that after a few minutes of diborane decomposition the concentration of B_5H_{11} will reach a steady state seems to be plausible.

Although Long mentions a low- and a high-temperature route of decomposition for B_5H_{11},[5] the experimental evidence about reaction products and possible intermediates, or about the rate of decomposition of B_5H_{11} by itself and in the presence of diborane, is too scarce to be useful for suggesting a suitable reaction mechanism. Further work is in progress.

[3/005 *Received, 19th April, 1973*]

---

[10] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, New York, 1969, p. 289.