1071. *The Pyrolysis of Decaborane.*

By A. J. Owen

The kinetics of the pyrolysis of decaborane have been investigated for a static system in the temperature range 210—250° and at decaborane pressures 60—600 mm. Hg. The decomposition leads to non-volatile solid hydrides and hydrogen; its rate is of the first order with respect to decaborane, slightly retarded by hydrogen; the activation energy is 41·6 ± 0·5 kcal./mole. Hydrogen is also formed by decomposition of the non-volatile solid hydrides, and its rate of formation in this way is strongly retarded by hydrogen. A mechanism for the formation of non-volatile solid hydrides is proposed and discussed.

The pyrolysis of decaborane to non-volatile solid hydrides and hydrogen was investigated as part of the general study of the synthesis of the higher boron hydrides from diborane. In previous work [1] it was suggested that the non-volatile solid hydrides produced during pyrolysis of diborane originated from decaborane. While it is known that they are formed at low temperatures (~100°) by the reaction of diborane with pentaborane [2] or decaborane [3] no information on the mechanism or reaction rates at the temperature (~240°) of pentaborane synthesis is available. The present work was therefore undertaken to supplement the knowledge of their formation.

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[1] Owen, *J. Appl. Chem.*, 1960, **10**, 483.

[2] Hillman, Mangold, and Norman, Abs. 133rd Meeting Amer. Chem. Soc., San Francisco, 1958, p. 18.

[3] Shapiro and Williams, *J. Amer. Chem. Soc.*, 1959, **81**, 4787.

The pyrolysis of decaborane was first described by Stock and Pohland[4] who found that it did not decompose appreciably at 200°, but did so extensively at 250°, to give non-volatile solids of approximate composition $(BH_{0·6})_x$. Beachell and Haugh[5] made a kinetic investigation of the system over the temperature range 170—238°, on the basis almost entirely of pressure measurements, from which they concluded that, in the initial stages, the reaction was of the first order with respect to diborane and was retarded by hydrogen. No detailed mechanism was proposed. Siegal and Mack[6] also studied the pyrolysis of decaborane; although their work was not intended to be of a kinetic nature, a plot of their results of time against percentage decomposition at 200° with an initial decaborane pressure of ~240 mm. gave a straight line, suggesting that the reaction was of zero order; but this will be shown to be due to their method of calculating the percentage decomposition from the hydrogen evolved.

EXPERIMENTAL

Pure decaborane, m. p. 99·7°, was obtained from an impure sample (American Potash and Chemical Co.) by crystallisation from hexane followed by vacuum-sublimation. By oxidation with potassium persulphate in alkaline solution and titration of the boric acid formed,[7] it was shown to have a purity of at least 99·5%. Hydrogen and "White Spot" nitrogen were obtained from cylinders and were dried.

Experiments were carried out in Pyrex reaction vessels having a total volume of ~150 c.c. They consisted of a reaction bulb, a freezing nipple, and an entry tube, 15 cm. long, comprising a B10 cone on the end of a 7 cm. stem of a B14 cone. Decaborane was introduced into the weighed reaction vessel of known volume by means of a funnel which prevented it from adhering to the side of the inlet tube. After weighing, the tubing between the glass joints was drawn down to a coarse capillary, and the reaction vessel connected to the vacuum line by the B10 joint, evacuated, and sealed at the top of the constriction. In the experiments on retardation by hydrogen and on alkylation, a known pressure of hydrogen or alkylating agent was admitted before the sealing. No detectable amount of decaborane was lost during this process.

The filled reaction vessels were placed in a well-stirred "Aroclor" bath, the surface of which was covered with pear-shaped glass globes to minimize the escape of the vapour. Electric fire-bars inserted in metal tubes in the bottom of the bath supplied heat to the bath. The temperature of the bath was controlled within ±0·5° by means of a bimetal switch in conjunction with an on-off Sunvic control operating on one of the fire-bars. Experiments were carried out for varying times at 210°, 230°, and 250° and initial decaborane pressures of 60, 120, 300, and 600 mm. Similar pressures of hydrogen were added in the retardation experiments. At the end of an experiment the reaction vessels were removed from the bath and rapidly cooled to room temperature, then connected, by means of the B14 ground-glass joint, to a seal-breaker on the vacuum line, and then opened.

Hydrogen was analysed by pressure-measurement after expansion of the gas into a known volume. The reaction vessel was then filled with dry nitrogen and removed from the vacuum line. Two methods, both giving identical results, were used to analyse the residue. Unchanged decaborane was (*a*) extracted from the solid products with dry benzene, or (*b*) sublimed from the evacuated vessel at 100°; in both cases the decaborane was subsequently estimated by the quinoline colorimetric method.[8] The reaction vessel containing the solid hydrides which remained after sublimation of the decaborane was connected by means of the B14 ground-glass joint to a mercury manometer of known volume and after evacuation heated to the reaction temperature; the rate of evolution of hydrogen was measured. Similar experiments were made with an initial hydrogen pressure equivalent to that developed in the main reaction of decaborane. Finally, the boron content non-volatile of the solid hydrides was determined by oxidation with alkaline persulphate.[7]

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[4] Stock and Pohland, *Ber.*, 1929, **62**, 90.

[5] Beachell and Haugh, *J. Amer. Chem. Soc.*, 1958, **80**, 2939.

[6] Siegal and Mack, *J. Phys. Chem.*, 1958, **62**, 373.

[7] Dunstan and Griffiths, M.O.A. unpublished report.

[8] Hill and Johnston, *Analyt. Chem.*, 1955, **27**, 1300.

RESULTS

The results are given in Figures 1—3.

Order of Reaction.—The course of the reaction is illustrated in Fig. 1 by a typical set of results obtained at 230° and an initial decaborane pressure of 300 mm. The decomposition of decaborane and the formation of hydrogen are shown by the lower and the upper continuous curve, respectively. The rate of decomposition of decaborane falls off gradually with time and the reaction is shown to be of the first order by first-order graphs (Fig. 2) drawn at 210°, 230°, and 250° over a range of initial decaborane pressures from 60 to 600 mm. Straight lines can only be drawn through points up to 60% reaction (corresponding to $\log [a/(a - x)] = 0{\cdot}4$). Above this conversion the reaction tends to be of greater than first order.

Decomposition of the non-volatile solid hydrides formed from decaborane also occurs and gives a polymeric material and hydrogen. This accounts for the fact that the rate of formation of hydrogen is much greater than that of decomposition of decaborane, especially in the later stages of the reaction, as illustrated in Fig. 1. It is probable that the non-volatile solid hydrides decompose according to a first-order law, since the hydrogen evolved at a given time is directly proportional to the initial pressure of decaborane.

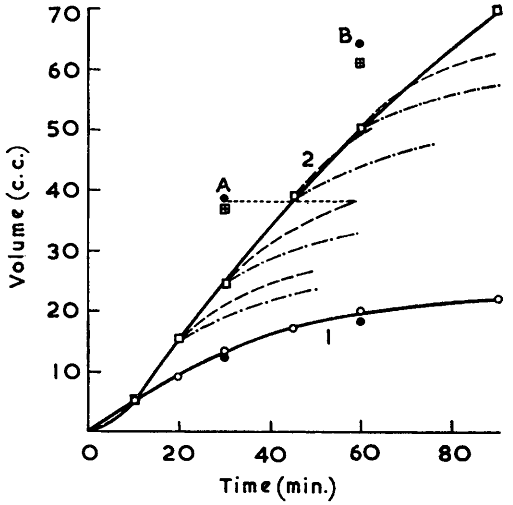

FIG. 1. Course of the decomposition of decaborane.

Temp. 230° C; $p^\circ_{B_{10}H_{14}} = 300$ mm.

1, Decaborane reacted.
2, Hydrogen formed.
—— Hydrogen formed from non-volatile solid hydride at $p^\circ_{H_2} = 0$.
—·— Hydrogen formed therefrom at $p^\circ_{H_2} = p_{H_2}$ in reaction.

Retardation by Hydrogen.—Examples of the retarding effect of hydrogen on (*a*) the rate of decomposition of decaborane and (*b*) the rate of formation of hydrogen are given in Fig. 3, where the volume of gas that reacted or was formed is plotted against the average pressure of hydrogen at 230°, with an initial decaborane pressure 300 mm. and reaction times of 10 and 30 min. After 10 min. the small retardation effect is almost identical for both the rate of decomposition of decaborane and the rate of formation of hydrogen. This would be expected if one molecule of decaborane decomposed to give one molecule of hydrogen, because in the early stages of the reaction the concentration of non-volatile solid hydrides is low and the rate of formation of hydrogen from them is small. In the later stages of the reaction, *i.e.*, after 30 min., the retardation is much more pronounced for hydrogen than for decaborane, owing to marked inhibition by hydrogen of the decomposition of the non-volatile solid hydrides.

The Activation Energy.—An Arrhenius plot leads to an activation energy of 41·6 ± 0·5 kcal./mole, in excellent agreement with the value of 41·4 kcal./mole obtained by Beachell and Haugh.[5]

Stoicheiometry of the Initial Steps.—It has already been pointed out that after a short initial reaction period hydrogen is produced much more rapidly than decaborane decomposes. Attempts were made to examine the rate of formation of hydrogen in the decomposition of the non-volatile solid hydrides alone, using hydrides which remained after the decaborane had been sublimed. The reaction vessel was connected to a manometer, evacuated, and heated at the reaction temperature for 30 min., the rate of gas evolution being followed on the manometer. The results are shown in Fig. 1 by the broken lines (---). They show that in the later stages of the decomposition of decaborane, *i.e.*, where there is a relatively large quantity of hydrides produced, the rate of formation of hydrogen in the complex overall reaction appears to be less than the rate of formation of hydrogen from the hydrides produced alone. The experiments were then repeated but extra hydrogen was added to the non-volatile solid hydrides so that the hydrogen pressure was that obtaining at the given time during the order experiments. The results of these experiments, shown as dot-dash curves (· —— · ——), indicate the marked inhibiting effect of hydrogen in the decomposition of the non-volatile solid hydrides. Comparison of the rates of formation of hydrogen from the non-volatile solid hydrides and that from the total reaction with the rate of decomposition of decaborane at 210°, 230°, and 250° (initial decaborane pressure 300 mm. and various reaction times) is given in the Table. The difference between the rate of formation of total hydrogen and the rate of decomposition of decaborane, d(H_2, total)/dt + d($B_{10}H_{14}$)/dt, is given almost exactly by the rate of evolution

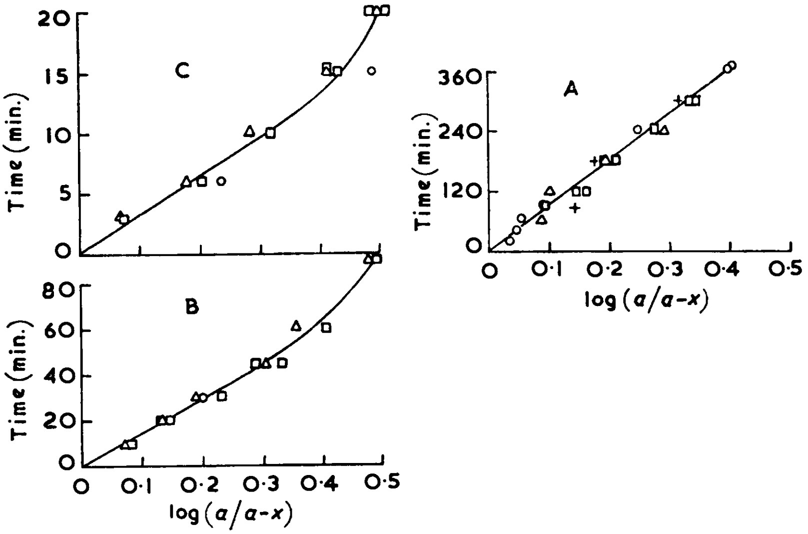

FIG. 2. Order of reaction with respect to decaborane at (A) 210°, (B) 230°, (C) 250°. ○, $p^{\circ}_{B_{10}H_{14}}$ = 600 mm. □, $p^{\circ}_{B_{10}H_{14}}$ = 300 mm. △, $p^{\circ}_{B_{10}H_{14}}$ = 120 mm. +, $p^{\circ}_{B_{10}H_{14}}$ = 60 mm.

Rate of formation of hydrogen from decaborane and non-volatile solid hydrides: initial pressure of decaborane = 300 mm.

Temp.	Time (min.)	$\frac{d(H_2)\text{ total}}{dt}$ (c.c./min.)	$\frac{-d(B_{10}H_{14})}{dt}$ (c.c./min.)	$\frac{d(H_2)\text{ total}}{dt} + \frac{d(B_{10}H_{14})}{dt}$ (c.c./min.)	$\frac{d(H_2)\text{N.V.S.H.}}{dt}$ No initial H_2 (c.c./min.)	Added H_2 (c.c./min.)
210°	120	0·138	0·083	0·055	0·083	0·060
	180	0·134	0·057	0·077	0·107	0·074
	240	0·117	0·042	0·075	0·107	0·074
	300	0·100	0·032	0·068	0·123	0·062
230	20	1·02	0·460	0·560	0·600	0·500
	30	0·950	0·375	0·575	0·620	0·500
	45	0·850	0·200	0·650	0·817	0·620
	60	0·650	0·110	0·540	0·666	0·507
250	3	5·15	2·32	2·83	2·3	2·2
	6	4·95	1·68	3·27	3·4	3·2
	10	3·55	0·83	2·72	—	2·6
	15	2·28	0·43	1·85	2·2	1·7
	20	1·85	0·29	1·56	2·0	1·4

of hydrogen from the non-volatile solid hydrides in the presence of the initially added pressure of hydrogen. It is significant that the rate of evolution of hydrogen from the non-volatile solid hydrides in the absence of initially added hydrogen approaches the other rates at low reaction times, *i.e.*, when there is only a relatively small quantity of hydride products and the initial hydrogen pressure is low. The initial step in the thermal decomposition of decaborane, therefore, requires that one molecule of hydrogen is formed for every molecule of decaborane decomposed: $xB_{10}H_{14} = (B_{10}H_{12})_x + xH_2$.

In order to gain a clearer picture of the reaction mechanism, decaborane and the non-volatile solid hydrides were heated together. The reaction vessels were modified in these experiments so that the entry tube was a double set of ground-glass joints, the outer set of joints being utilised in obtaining a sample of non-volatile solid hydride as a surface coating inside the reaction vessel. This sample was prepared by heating 300 mm. decaborane at 230° for 30 min. The second set of joints was utilised when more decaborane was weighed into the reaction vessel to return the decaborane pressure to 300 mm. The non-volatile solid hydrides were thus never handled and were subjected only to dry nitrogen during the weighing. The durations of these experiments at 230° were 30 and 60 min. and the results are plotted in Fig. 1 by the points ⊕ and ⊞ which represent the decaborane decomposed and the hydrogen formed, respectively.

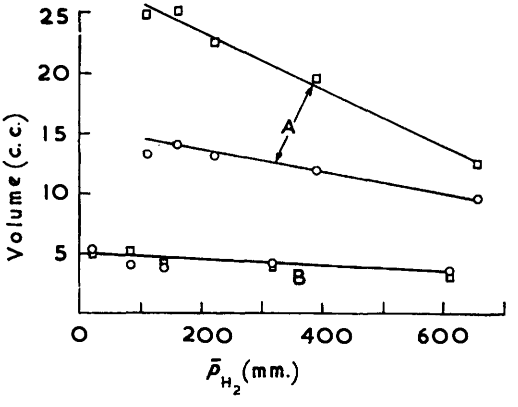

FIG. 3. Hydrogen retardation. 1, Reaction time (A) 30 min, (B) 10 min. ○, Decaborane reacted; □ hydrogen formation.

The amount of decaborane decomposed is very close to that decomposed in the absence of non-volatile solid hydrides, the slightly lower values being consistent with a small retardation due to the increased hydrogen pressure developed by the hydrides produced. Although the hydrogen evolved is much less than the theoretical points A and B (obtained by addition of the hydrogen evolved from the initial non-volatile solid hydrides to the hydrogen normally produced in the decomposition experiments for reaction times of 30 and 60 min., respectively), the result is consistent with the retarding effect of hydrogen on the hydrogen evolution from the non-volatile solid hydrides. These two experiments show that the reaction of decaborane with the solid hydrides produced from it is so slow that it need not be considered in the proposed reaction mechanism.

DISCUSSION

Reaction Mechanism.—The following mechanism is proposed to explain the experimental facts.

$$B_{10}H_{14} + B_{10}H_{14} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B_{10}H_{14}^* + B_{10}H_{14} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$B_{10}H_{14}^* \underset{k_4}{\overset{k_3}{\rightleftharpoons}} B_{10}H_{12} + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$B_{10}H_{14} + B_{10}H_{12} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} B_{20}H_{24} + H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$B_{20}H_{24}(g) \rightleftharpoons B_{20}H_{24}(s) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$2B_{20}H_{24} \rightleftharpoons H_2 + \text{Non-volatile solid hydrides} \quad . \quad . \quad . \quad . \quad (5)$$

In the steady state, assuming $k_3 \ll k_2[B_{10}H_{14}]$, we have

$$-\frac{d[B_{10}H_{14}]}{dt} = k_5[B_{10}H_{14}][B_{10}H_{12}] - [H_2](k_4[B_{10}H_{12}] + k_6[B_{20}H_{24}]) \quad . \quad (6)$$

Since it has been shown experimentally that hydrogen has only a small effect on the rate of reaction of decaborane, the hydrogen retardation term can be neglected. If the rate of reaction of the intermediate $B_{10}H_{12}$ with decaborane is faster than the other reactions, the rate-determining step will be the formation of the intermediate which is given by the expression

$$\frac{d[B_{10}H_{12}]}{dt}\text{ formation} = \frac{k_1k_3}{k_2}[B_{10}H_{14}] + \frac{k_3k_4}{k_2}\cdot\frac{[B_{10}H_{12}][H_2]}{[B_{10}H_{14}]}$$

$$\simeq \frac{k_1k_3}{k_2}[B_{10}H_{14}]$$

Under these conditions the reaction is of first order with respect to decaborane.

As the reaction proceeds the concentration of decaborane decreases, and it can be shown that for suitable values of k_5 and k_1k_3/k_2, the rate of formation of the intermediate $B_{10}H_{12}$ will become closer to the rate of its subsequent reaction with decaborane. Eventually the term $k_1k_3[B_{10}H_{14}]/k_2$ will be greater than $k_5[B_{10}H_{14}][B_{10}H_{12}]$ and will result in deviations from the first-order expression. These deviations should be greatest in the experiments carried out at the lower initial decaborane pressures. Unfortunately, the experimental error is too large for the effect of variation of initial decaborane pressures to be seen in Fig. 2.

The decomposition of the non-volatile solid hydrides represented by equation (5) is very complex, and no detailed examination of this reaction was made in the present work. However, the retardation of the hydrogen evolution from those hydrides by hydrogen, originally observed by Shapiro and Williams,[3] is interesting. Since the effect is restricted to hydrogen,[5] the reaction must be to some extent reversible. It is conceivable that the polymer, on heating, loses hydrogen and becomes a free radical. Subsequently the radicals could either recombine with the hydrogen, or irreversibly dimerise. This speculative reaction would account for the observed kinetic phenomenon.

The results quoted in this paper are in qualitative agreement with those of other workers.[5,6] Quantitatively, however, the hydrogen-retardation effect on the rate of decomposition of decaborane is much smaller than that reported by Beachell and Haugh.[5] For example, in their work, the rate constant at 220° and a decaborane pressure of 268 mm. decreased linearly from $9{\cdot}8 \times 10^{-3}$ min.$^{-1}$ at zero initial hydrogen pressure to $3{\cdot}0 \times 10^{-3}$ min.$^{-1}$ at 600 mm. initial hydrogen pressure. The nearest corresponding conditions in the present work were at 230° and a decaborane pressure of 300 mm., when the rate constant decreased from $1{\cdot}60 \times 10^{-2}$ to $1{\cdot}16 \times 10^{-2}$ min.$^{-1}$ for the corresponding hydrogen pressures. Obviously the discrepancy has arisen through the different methods of analysis employed in the two studies. In fact, Beachell and Haugh have stated that their rate constants were calculated from the pressure measurements of " all boron hydridic materials (P_{BH})." It is possible that the intermediate $B_{20}H_{24}$ proposed for the present reaction mechanism would appear in greater concentration when the pressure of initial hydrogen is increased and thus magnify the true retardation effect on the rate of decomposition of decaborane.

Siegal and Mack's results[6] are misleading because the values they give for the percentage decomposition of decaborane are based on the amount of hydrogen evolved and the wrong assumption that a constant 2 molecules of hydrogen are evolved for each molecule of decaborane decomposed. Thus, a plot of the percentage decaborane decomposed against time would lead to a graph very similar in shape to that given by the hydrogen curve in Fig. 1, and not inconsistent with the zero-order kinetics mentioned previously.

The proposed mechanism accounts for all the available experimental results. Beachell and Haugh[5] have shown that hydrogen radicals do not participate in the reaction and it has therefore been assumed that the first step leads to the splitting off of a hydrogen molecule. Using the infrared absorption bands for various pyrolysis products they showed also that the initial hydrogen break did not involve a bridge hydrogen atom, but they were uncertain of the site at which the break occurred. However, comparison of the reaction of decaborane and ethyl bromide with the pyrolysis of decaborane under similar conditions (230° with a reaction time 5 min. and decaborane pressure 300 mm.) gave an almost identical conversion of decaborane (8%). In the alkylation experiment the product consisted of 2-ethyldecaborane and a trace of non-volatile solid hydrides, which suggests that the initial step in the decomposition of decaborane involves the breaking of the 2-BH bond. Further work on the kinetics of the alkylation of decaborane is in hand to test this view.

Additional evidence indicating that the initial break involves the 2-position has been obtained during an attempt to isolate the intermediate product $B_{20}H_{24}$. Vacuum sublimation at 100° of the solid products prepared at 230° enables all the unchanged decaborane to be removed, and subsequent vacuum distillation at 210° afforded a very small quantity of a viscous liquid. This liquid has an infrared spectrum very similar to that of decaborane but has such a low volatility that it was not recovered from a 3-ft. gas-chromatographic column[9] even after 7 hours. It is therefore believed to be the $B_{20}H_{24}$ intermediate. For material of this high molecular weight to exist as a liquid at room temperature, its structure would be expected to be highly unsymmetrical, possibly joined between the 2- and the 6-positions; it should not be the eicosahedron previously suggested to account for the impurity lines in the mass spectrum of decaborane.[10]

One of the objects of this work was to see if the decomposition of decaborane made any significant contribution towards the formation of non-volatile solid hydrides on pyrolysis of diborane at ~240°. It can be shown that at 240°, with 1 : 5 diborane : hydrogen, total flow rate 400 c.c./min., in a 12-unit multistage pyrolyser,[1] only about 0·1% of decaborane is converted by thermal decomposition alone into non-volatile solid hydrides. This is considerably less than is observed in practice,[1] and it is probable that the solid non-volatile hydrides formed during the pyrolysis of diborane originate in a reaction of diborane with decaborane.[3]

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