

hexafluoride as an added "inert" gas are subject to some question. But however disturbing, the observed effect of this gas on the photolysis of pure ketene itself, being in the opposite direction to the effect it has on the reformation of ketene, does not weaken the interpretation of its acting as a third body by reaction (5).

The ratio $k_5/k_4 = 0.8$ for the relative efficiencies of sulfur hexafluoride and ketene shows that sulfur hexafluoride is almost as good as a third body as ketene itself.

As nitrogen definitely does not react with methylene, it can be safely considered as an inert gas. The scatter of the individual values of the ratio k_5/k_4 listed in Table IV is very large, but they are all positive, and their average $k_5/k_4 = 0.1$ demonstrates that nitrogen does increase the rate of the reaction of methylene with carbon monoxide. Its efficiency is however low compared to ketene or sulfur hexafluoride. This finding justifies, *a posteriori* and by analogy, the omission of a third body effect of carbon monoxide in equations 6 and 7.

The average value of the ratio of rate constants

k_3/k_4 , given by the two methods used, is 10.5 mm. This value is of the order of magnitude of what could be expected for the association reaction of molecules of the size of CH_2 and CO , but is somewhat smaller than might have been predicted, since it is only about four times larger than the ratio of corresponding rate constants determining the formation of ethane from methyl radicals. Ethane has 17 vibrational degrees of freedom whereas ketene has only 9; yet the value of k_3/k_4 suggests that the lifetime of the activated ketene molecule is only about one-fourth that of the activated ethane.

Finally, it is interesting to note that the rate constants of the reactions of methylene with ketene, with carbon monoxide and with ethylene are of the same order of magnitude.

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The Pyrolysis of Decaborane¹

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Rate constants for the homogeneous first-order disappearance of decaborane in vapor phase pyrolysis were obtained over the range 170–238°, and an activation energy of 41.4 kcal. was calculated. Inhibition by hydrogen, but not by other gases was shown. Comparison of the rates for decaborane and deuterio-decaborane indicated that the rupture of B–H or B–D bonds was rate determining. Decaborane was also found to disappear by a rapid polymerization reaction without immediate loss of hydrogen to form an intermediate polymer consisting of decaborane-like units. This was followed by further loss of hydrogen and molecular weight increase with cross-linking to yield non-volatile solid hydrides. No products or intermediates more volatile than decaborane were observed. Evidence for the presence of free radical intermediates and absence of hydrogen atoms was interpreted as indicating an initial split of molecular hydrogen with formation of a diradical intermediate. Hydrogen was found to split out preferentially at the external B–H bonds initially, rather than at the bridged hydrogen positions. The pyrolysis of diiodo-decaborane was shown to yield only hydrogen and non-volatile solid products.

Introduction

The pyrolysis of decaborane was first described qualitatively by Stock and Pohland,² but the kinetics and mechanism of this reaction so far have not been reported. The purpose of this work was to determine the kinetics and mechanism of the initial reaction by which decaborane disappears in vapor phase pyrolysis, and to investigate the nature of the reactions forming the solid, non-volatile boron hydrides, which, with hydrogen, are the sole products of decaborane pyrolysis. Similar non-volatile products also occur during pyrolysis of the lower members of the volatile boron hydrides series, in addition to the principal volatile products.^{3–5}

Experimental

Apparatus.—Kinetic measurements and vapor pressure determinations were made in an all glass apparatus which

incorporated a glass manometer diaphragm and pointer such as described by Daniels,⁶ sealed in a section of 25 mm. Pyrex tubing, 10–11 inches in length, dividing it into two parts. In the sample chamber (approximately 3 inches in length) decaborane or other material could be sealed *in vacuo*, or in the presence of gases. The balancing chamber was connected through a stopcock to an external mercury manometer system with which pressures in the sample chamber could be measured indirectly by matching pressures so that the pointer would be at a reference position previously determined with both ends of the apparatus open to the atmosphere.

Samples for infrared analysis were prepared in ampoules made from 25 mm. Pyrex tubing with smaller ampoules of 8 mm. tubing attached. Intermediate pyrolysis products could be washed into these smaller ampoules and separated from the unreacted decaborane by repeated sublimation and melting of the decaborane.

Heating, in most cases, was done with a molten salt or wax bath. Where temperature control was not critical, a tubular electric furnace was used. For kinetic measurements, bath temperatures were regulated to $\pm 0.2^\circ$ with standard thermoregulators.

Materials. Decaborane.—Pure decaborane (m.p. 99.7°) was obtained by recrystallizing the crude material resulting from diborane pyrolysis. This purified material was stored in a vacuum desiccator.

(1) Taken from the Ph.D. thesis by John F. Haugh, submitted to the faculty of the University of Delaware, June, 1957.

(2) A. Stock and E. Pohland, *Ber.*, **62B**, 90 (1929).

(3) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(4) H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1 (1942).

(5) F. G. A. Stone, *Quart. Revs.*, **9**, 174 (1955).

(6) F. Daniels, *This Journal*, **50**, 1115 (1928). The diaphragm was similar to type No. 4 in the Figure on p. 1116.

Deutero-decaborane.—A small sample of completely deuterated decaborane was prepared by pyrolysis of deutero-diborane, B_2D_6 , and purified by recrystallization.

Diiodo-decaborane.—Diiodo-decaborane was prepared by a sealed tube reaction of decaborane and iodine at 100° , after the method of Stock,⁷ and purified by recrystallization.

The samples of propylene, hydrogen, nitrogen, argon and helium gases, and antimony metal were all of reagent grade purity.

Procedure.—In preparing a sample of decaborane for pyrolysis, an amount approximately 20% in excess (to allow for loss in transfer and pumping) of that required to give a desired initial pressure at the pyrolysis temperature with all the decaborane in the vapor phase, was weighed out on a small piece of filter paper, and washed into the apparatus through a small funnel with purified anhydrous pentane or heptane. This procedure served to further purify the sample in case any decomposition had occurred during storage, and also provided a convenient method of getting the sample through the small opening in the apparatus. The solvent was then pumped off, and the apparatus was evacuated to a pressure of 3×10^{-5} mm., the sample chamber being jacketed with ice to prevent loss of the volatile decaborane. After about 15 minutes pumping, the sample chamber was sealed off using a gas-oxygen torch. By using the external manometer system, measured pressures of various gases could be sealed into the apparatus with the decaborane.

Rate measurements were made by heating the apparatus in a constant temperature bath, and measuring total pressures with time. The apparatus was removed from the heating bath periodically, and cooled in ice. The pressure of hydrogen evolved was then measured, the vapor pressures of decaborane and the pyrolysis products being negligible at 0° .

In the runs with propylene, hydrogen pressures were measured at liquid nitrogen temperature. Subtracting the calculated hydrogen pressures from the measured total pressures at 0° gave the pressures of propylene.

Pyrolysis products other than hydrogen were found to contribute negligibly to the total pressures at reaction temperatures, so that for rate calculations, the partial pressure of decaborane was considered, as a good approximation, equal to the partial pressure of all boron hydride materials (P_{BH}), *i.e.*, the difference between the calculated pressures of hydrogen and other gases, and the measured total pressures at pyrolysis temperatures.

Molecular weight determinations on the pyrolysis products were made from vapor pressure measurements. Decaborane was pyrolyzed at 200° , and hydrogen pressures were measured at 0° in the usual manner. In addition, pressures were measured at an intermediate temperature (150°) at which the decaborane in the system was mostly condensed as a liquid. Molten decaborane was found to be a fairly good solvent for the pyrolysis products, and these were washed down into the tip of the apparatus by successively subliming and melting the decaborane. When a homogeneous solution was obtained, and equilibrium established, the total pressure at 150° was measured. Subtraction of the calculated H_2 pressure gave the vapor pressure of the solution of pyrolysis products in liquid decaborane.

Results and Discussion

Rate Studies.—Kinetic measurements were made over the temperature range 170 – 238° , and rate constants for the disappearance of decaborane in vapor phase pyrolysis are given in Table I. Calculation of these rate constants was based on P_{BH} values determined as described above.

Decaborane pyrolysis at temperatures below 170° was studied only qualitatively as rates were very slow. Heating samples of decaborane at 140° for 24 hours, and at 150° for 20 hours, gave no measurable amounts of hydrogen. However, heating for 22 hours at 160° gave about 2 mm. hydrogen pressure, measured at 0° , from an initial decaborane pressure of 180 mm.

(7) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 121.

TABLE I
FIRST-ORDER RATE CONSTANTS FOR THE DISAPPEARANCE OF
DECABORANE IN VAPOR PHASE PYROLYSIS

t , °C.	P_0 , mm.	k_0 , min. ⁻¹
237.8	325	4.41×10^{-2}
220.5	161	9.35×10^{-3}
220.4	268	9.86×10^{-3}
210.6	430	5.04×10^{-3}
210.5	486	5.03×10^{-3}
210.6	118	4.33×10^{-3}
200.0	426	1.80×10^{-3}
200.4	527	1.58×10^{-3}
170.2	206	8.65×10^{-5}

The disappearance of decaborane during pyrolysis was shown to be a homogeneous vapor phase process, as no change in rate was observed when large increases in the surface to volume ratio were effected by packing the apparatus with glass wool.

The change in decaborane pressures during reaction was found to follow closely the first-order rate equation, as determined by calculations with the quarter, half and three-quarter life time values for the decrease of P_{BH} in runs with different initial decaborane pressures. Actual values for n were 1.1–1.2.

However, when the log of decaborane pressure, or more correctly $\log P_{BH}$, was plotted against time, a straight line relationship was not observed as expected for a first-order reaction. Instead, a smooth curve was obtained with maximum slope at zero time. Nevertheless, the tangent slope at any time could be measured, and "instantaneous" rate constants determined by the equation

$$k_{inst} = -2.303(d \log P_{BH}/dt)$$

Values for k_{inst} were found to vary linearly with the hydrogen pressure, becoming smaller as the hydrogen pressure increased. Plotting k_{inst} against hydrogen pressure, and extrapolating to zero pressure gave k_0 values which could be regarded as the true first-order rate constants for the process. This was the method used to determine the values given in Table I. The effect of hydrogen pressure on the rate of disappearance of decaborane in pyrolysis may be expressed by a linear equation

$$k_{inst} = (d k_{inst}/d P_{H_2})P_{H_2} + k_0$$

This relationship is illustrated in Fig. 1.

The activation energy for the disappearance of decaborane was found to be 41.4 kcal., as calculated from the k_0 values in Table I. Other reactions in the over-all pyrolysis process were regarded as too complex for kinetic analysis with available information.

The retarding effect of hydrogen was shown to be unique by making a series of runs in which initial pressures of hydrogen and other gases were sealed in the apparatus with the decaborane. Here the k_0 values were determined at the time of zero hydrogen pressure developed by the reaction, exclusive of hydrogen put in initially. The results, summarized in Table II, show that the presence of hydrogen caused a marked decrease in rate, whereas the other gases had no effect. In line with the relationship between rate and hydrogen pressure discussed above, the k_0 values in the runs where initial pressures of hydrogen were present

TABLE II

THE EFFECT OF INITIAL PRESSURES OF VARIOUS GASES ON THE RATE OF DECABORANE PYROLYSIS AT 220°

$P_0(\text{B}_{10}\text{H}_{14})$, mm.	Gas	P_0 (gas), mm.	$k_0 \times 10^3$, min. ⁻¹
138	None	..	10.1
191	H ₂	385	5.9
102	H ₂	594	4.5
128	N ₂	610	9.9
122	He	640	10.1
135	A	600	9.7

were also seen to vary linearly with the initial hydrogen pressures. This inhibition of pyrolysis by hydrogen only, suggests that the initial split of hydrogen may be a reversible reaction. However, no evidence was obtained that hydrogen reacted with any of the pyrolysis products to give decaborane. The presence of hydrogen has been shown to affect the rate of diborane pyrolysis also.⁸

The pyrolysis of deuterio-decaborane was considerably slower than that of ordinary decaborane. The first-order rate constant was found to be 6.65×10^{-3} min.⁻¹ at 229°. The rate constant calculated for decaborane at that temperature is 2.7 times as great. This isotope effect indicates that B-H or B-D bond rupture is rate determining. However, it will be shown by stoichiometric and molecular weight measurements that decaborane also disappears in a rapid polymerization reaction without immediate loss of hydrogen. Thus the rate constants obtained are for the over-all disappearance of decaborane without regard to the mode of reaction.

Stoichiometric Measurements.—The over-all stoichiometry for the pyrolysis of decaborane as determined from the final pressure of hydrogen, and the initial decaborane pressure was found to be 3.7–3.8 moles of hydrogen per mole of decaborane used. This agrees with the empirical formula $\text{BH}_{0.6}$ determined by Stock and Pöhlend² for the final products of pyrolysis at 250°. However, this stoichiometry did not hold throughout the reaction. Values started off as low as 0.25 in the early stages of pyrolysis at 200°, then increased gradually, finally levelling off at 3.7–3.8 moles of hydrogen per mole of decaborane, as determined at higher temperatures.

As a consequence of these low stoichiometries, the total pressure during the initial periods of pyrolysis was found to drop significantly. For example, at 200° the pressure dropped to approximately 90% of the initial value. After four hours enough hydrogen pressure was developed to bring this total pressure back up to the initial value, after which a steady increase was observed.

Molecular Weight Determinations.—An explanation for the low initial stoichiometries observed is given by the molecular weight studies. Values for the average molecular weight of products in the earlier stages of pyrolysis at 200°, as determined by vapor pressure lowering measurements, are given in Table III. The molecular weight is seen to have risen rapidly to the vicinity of 600 after about 40 minutes, and then to have increased slowly. A suggested explanation is that an active

(8) R. P. Clarke and R. N. Pease, *THIS JOURNAL*, **73**, 2132 (1951).

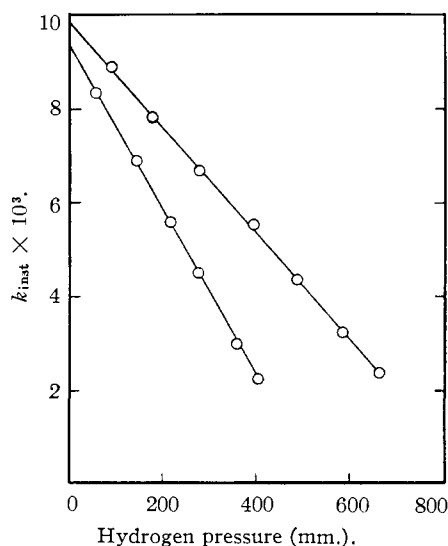


Fig. 1.—The relationship between hydrogen pressure and instantaneous rate constants for the disappearance of decaborane during pyrolysis at 220° (cf. Table I): upper plot, $P_0 = 268$ mm.; lower plot, $P_0 = 161$ mm.

boron hydridic radical fragment, resulting from an initial splitting out of hydrogen, could join onto other decaborane molecules without immediate loss of hydrogen in a manner analogous to initiated vinyl polymerization. This process would then be followed by further loss of hydrogen, with gradual increase in molecular weight.

TABLE III

THE RISE OF THE AVERAGE MOLECULAR WEIGHT OF THE PRODUCTS OF DECABORANE PYROLYSIS WITH TIME, FROM VAPOR PRESSURE LOWERING MEASUREMENTS

First determination <i>t</i> , min.	Av. mol. wt.	Second determination <i>t</i> , min.	Av. mol. wt.
13	375	20	495
30	531	50	634
60	648	80	698
105	711	120	745
160	781	160	781
200	816	200	835
300	915		

Infrared Analysis of Pyrolysis Products.—Support for such a polymerization reaction was gained from infrared analysis. A Baird Associates, Model B, recording infrared spectrophotometer was used in this study. For products of 2, 5 and 10 hours pyrolysis at 200°, the over-all appearance of the spectra was very similar to that of decaborane, except for a general broadening of the bands in the 9–16 μ region, the disappearance of a band at about 13.4 μ , and the appearance of a new band at 12.5 μ . This similarity suggests that the initially formed polymeric materials consisted essentially of decaborane-like units. The over-all appearance of the spectra of the final products of pyrolysis at 238°, however, was quite different. Hardly any well-defined bands were observed in the 9–16 μ region, suggesting a highly cross-linked polymeric material.

It was further shown that there were no pyrolysis products or intermediates more volatile than

decaborane, that is, which may have resulted from breaking up of the decaborane framework. The products, which ranged in appearance from colorless, to brown, and yellow-brown glassy solids, for intermediate products, and whitish-yellow amorphous solids spotted with glassy brown materials for final products, were non-volatile at room temperature, although some whitish materials formed initially in trace amounts were slightly volatile, and could be sublimed with gentle warming.

Evidence for Free Radical Intermediates.—The presence of free radical intermediates in the pyrolysis of decaborane was demonstrated by reaction with propylene. A large uptake of propylene was observed, although tests for free hydrogen atoms were negative. Thus the evidence available suggested the split of molecular hydrogen initially, with the formation of a boron hydridic diradical. A molecular split would be favored energetically, since if the formation of a hydrogen molecule were involved in the initial bond rupture, its large energy of formation could be expected to aid the split.

Tests for free hydrogen atoms during reaction were made by pyrolyzing decaborane in a flow system in the presence of antimony mirrors after the method of Paneth and Hofeditz.⁹ In spite of extensive decomposition over the range 300–420°, no removal of mirrors was observed whatever, thus indicating the absence of free hydrogen atoms.

The presence of boron-hydridic free radical fragments was demonstrated by pyrolysis of decaborane at 200° in the presence of propylene. A large and fairly rapid uptake of propylene was observed, along with a decrease in the rate of disappearance of decaborane, and an increase in the rate of hydrogen evolution. Small amounts of an oily material, and traces of a liquid of intermediate volatility were isolated from the reaction products. Both of these were shown to be essentially hydrocarbon in nature by the presence of a small C–H stretching band in their infrared absorption spectra. No other bands of significance were observed with the small amounts of material available. No bialllyl was found in the products, as might have been expected from the generally accepted mechanism for inhibition by propylene.¹⁰ The most likely explanation, in view of the foregoing considerations, is that boron hydridic free radicals initiated some polymerization of the propylene.

Preferred Sites for the Split of Hydrogen.—Hydrogen was shown to split out preferentially at the external B–H bonds initially, rather than at the bridged hydrogen positions. This might be predicted from the observations by Kaufman and

(9) F. Paneth and W. Hofeditz, *Ber.*, **62B**, 1335 (1929).

(10) H. E. de la Mare and W. E. Vaughan, *J. Chem. Educ.*, **34**, 11 (1957).

Koski¹¹ that deuterium exchange between decaborane and deuterio-decaborane at 100° occurs exclusively with the non-bridge hydrogens.

In this study, the infrared absorption bands for the products from 2, 5 and 10 hours pyrolysis at 200° were compared with those of decaborane. For the spectrophotometer used, the resolution was such that the absorption for decaborane in the 2–7 μ region was one strong, fairly narrow band at 3.9, a weak, broad shouldered band at about 5.3, and a medium strong, broad shouldered band at about 6.7 μ . By the assignments of Keller and Johnston,¹² the absorption at 3.9 μ was due to external B–H stretching, and that at 5.3 and 6.7 μ to the B–H · · B bridge bonds. For the samples analyzed, a general decrease in intensity of the 3.9 μ band, relative to the other two bands, as the degree of pyrolysis increased, indicated that initially, at least, the external B–H bonds did split preferentially.

However, the final products of pyrolysis at 238° showed a fairly strong B–H stretching absorption relative to the other frequencies, indicating that some attack on the bridged hydrogens may have occurred at advanced stages in the pyrolysis reaction.

Speculation as to which of the external B–H bonds are most likely to rupture initially can be made by consideration of the structure of diiodo-decaborane. The valence studies of Lipscomb¹³ led to the possibility of predicting that the B_{III} positions are the most susceptible to attack in substitution reactions to form dihalides. Schaeffer¹⁴ in his studies on the molecular structure of diiodo-decaborane has shown that the B_{III} positions are indeed substituted. By analogy it is suggested that at least one, if not both, the apical B_{III} positions may be involved in the initial split of hydrogen in decaborane pyrolysis.

However, no iodine or hydrogen iodide was liberated in the pyrolysis of diiodo-decaborane at 229°. Hydrogen and non-volatile solids were the only products. The same final stoichiometry was found as for decaborane, that is, 3.7 moles of hydrogen per mole of diiodo-decaborane reacted. At 229°, the diiodo-decaborane was only partially vaporized, so that no significant rate data for comparison with decaborane were obtained.

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(11) J. J. Kaufman and W. S. Koski, *THIS JOURNAL*, **78**, 5774 (1956).

(12) W. E. Keller and H. L. Johnston, *J. Chem. Phys.*, **20**, 1749 (1952).

(13) W. N. Lipscomb, *J. Phys. Chem.*, **61**, 23 (1957).

(14) R. Schaeffer, Division of Physical and Inorganic Chemistry, The American Chemical Society, Abstracts of Papers presented at Cincinnati, Ohio, March 29–April 7, 1955, p. 37-Q.