Table VI. Values of the Parameters That Were Derived for Various Categories of Compounds

Parameter	Alkanes	Alcohols I	Alcohols II	Aldehydes	Carboxylic acids	Esters
A	18.318		17.430		16.018	16.087
B	11.260		11.383		11.925	11.706
C	0.570		0.920		1.056	0.289
D		4.760	4.998			
E		1.263	1.098			
F				−6.030		
G				0.180		
P					31.010	
H						42.894
I						0.457
J						−0.935

information for an exact calculation, and we feel that attempts at approximation are probably unreliable.

Finally, we feel that our present considerations contain the guidelines for a theoretical description of the diamagnetic susceptibilities of all organic molecules. For practical reasons we have limited the discussion to saturated, oxygen-containing organic compounds, but it is easily seen that similar discussions can be presented for other categories of organic compounds. Because of the accuracy of the theoretical results, so that even small variations in susceptibilities between different isomers are accounted for, we feel that such discussions may lead to an increase in understanding of the details of chemical structure.

Acknowledgment. We wish to express our gratitude to Dr. George W. Smith of General Motors Corporation for supplying us with his compilation of diamagnetic susceptibilities of organic molecules.

Kinetics of the Decomposition of Tetraborane(10)

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Abstract: The decomposition of tetraborane(10) has been studied at 40, 50, and 60° and at pressures of 37, 73, and 110 Torr at each of these temperatures. The course of the reaction was followed by the periodic analysis of the mixture for tetraborane(10), diborane, pentaborane(9), and pentaborane(11). The reaction is $^3/_2$ order in tetraborane(10) at each temperature and pressure except for the 60° runs at the two lower pressures. In these cases the decomposition appears to be approaching first-order behavior.

Excellent bibliographies of the thermal decomposition of various boron hydrides may be found in several books.[1-5] The studies dealing primarily with the decompositions of tetraborane(10) are those of Pearson and Edwards,[6] Dupont and Schaeffer,[7] and Baylis, Pressley, Gordon, and Stafford.[8]

Pearson and Edwards studied the pyrolysis of tetraborane(10) at temperatures of 60, 80, and 100° and found that the rate of decomposition of tetraborane(10) was first order. Decomposition products were diborane, pentaborane(11), hydrogen, a yellow solid, and lesser amounts of pentaborane(9), decaborane, and hexaborane(12). Copyrolysis of diborane and tetraborane(10) resulted in the production of relatively large amounts of pentaborane(11), and the rate of decomposition of tetraborane(10) appeared to be independent of the concentrations of diborane and of pentaborane(11). These authors suggest that tetraborane(10) decomposes by two simultaneous first order paths involving, respectively, B_3H_7 and B_4H_8 intermediates.

Dupont and Schaeffer studied the decomposition of mixtures of diborane and tetraborane(10) at temperatures 70–90°. The rate of the reaction was first order in tetraborane(10) and independent of the diborane pressure. The study appears to support a mechanism in which B_4H_8 is produced by the loss of hydrogen.

The work of Baylis, *et al.*, differs from the above studies in that the data were obtained by the use of a mass spectrometer. A B_4H_8 fragment was detected in the low-pressure pyrolysis at temperatures from 10 to 285° and nearly all known boron hydrides including decaborane were found. No conventional kinetic analysis of the data obtained in this study is possible.

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(1) R. T. Holzmann, "Production of Boranes and Related Research," Academic Press, New York, N. Y., 1967.

(2) E. L. Muetterties, "The Chemistry of Boron and Its Compounds," John Wiley and Sons, Inc., New York, N. Y., 1967.

(3) R. M. Adams, "Boron, Metallo-Boron Compounds and Boranes," John Wiley and Sons, Inc., New York, N. Y., 1964.

(4) W. N. Lipscomb, "Boron Hydrides," Benjamin, New York, N. Y., 1963.

(5) R. F. Gould, "Borax to Boranes," Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961.

(6) R. K. Pearson and L. J. Edwards, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1957.

(7) J. A. Dupont and R. Schaeffer, *J. Inorg Nucl. Chem.*, **15**, 310 (1960).

(8) A. B. Baylis, G. A. Pressley, Jr., M. E. Gordon, and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 929 (1966).

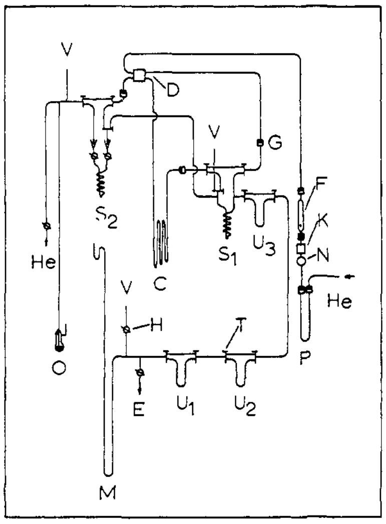

Figure 1. Schematic of analytical apparatus: V, to high vacuum; D, Gow-Mac Microcell JDC 133; G, metal to glass connections; S_1 and S_2, glass spirals; F, flow meter; K, check valve; N, 10 turn needle valve; U_1, U_2, U_3, sample holding U tubes; E, sample entry port; C, open tubular column; M, capillary manometer; O, mercury bubbler.

Since significant decomposition of tetraborane(10) occurs even at room temperature, we selected for our work temperatures from room temperature to 60°. Decomposition of products obtained in the primary B_4H_{10} decomposition is less important at the lower temperatures so that there is a better chance of sorting out the reactions due primarily to the initial processes. The method of analysis employed also minimized the effects of secondary decompositions of unstable products, and enabled us to follow the reaction by direct and quantitative analysis of the mixture for B_4H_{10}, B_2H_6, B_5H_9, and B_5H_{11}. Hydrogen and nonvolatile solids can be determined indirectly.

Experimental Section

Tetraborane(10) was prepared by essentially the method of Schaeffer and Tebbe.[9] In a typical preparation, 0.8 g of $NaBH_4$ and 8.0 cc of spectroquality diglyme dried over $LiAlH_4$, were placed in a 180-cc reaction tube previously filled with dry N_2 gas. The tube was then attached to the high-vacuum apparatus by means of a side arm containing a pressure stopcock and standard taper. The tube through which the reactants had been introduced was sealed off. The reactants were frozen with liquid nitrogen, the tube evacuated, and 342 cc of B_2H_6 was condensed into the tube. The stopcock was closed and the tube removed from the vacuum line and allowed to warm to room temperature. The lower part of the tube was then immersed in an oil bath at 100° for about 1 hr, or until hydrogen evolution had ceased. After cooling to room temperature the tube was again attached to the vacuum line and all volatile products were removed. In addition to hydrogen, 2.6 cc of B_2H_6 and the major portion of the diglyme were recovered. It is impossible to quantitatively remove diglyme from the NaB_3H_8 produced in this reaction. On the basis of B_2H_6 consumed 15 mmol of NaB_3H_8 was produced according to the reaction $NaBH_4 + B_2H_6 \rightarrow NaB_3H_8 + H_2$. Onto the residue in the tube, 339 cc of B_2H_6 and 335 cc of HCl were condensed, and the tube was then warmed to 0° for approximately 40 min. The tube was opened to the vacuum line and the B_4H_{10} was purified, as determined by our analytical system, by conventional techniques. The pure B_4H_{10} produced in this reaction amounted to a 40% yield on the basis of the reaction $4HCl + 4NaB_3H_8 \rightarrow 3B_4H_{10} + 4NaCl + 3H_2$. The B_2H_6 added with the HCl in the second step of the preparation was nearly always recovered quantitatively. Its omission in a subsequent B_4H_{10} preparation gave essentially the same yields and avoids the possible HCl contamination of rather large quantities of B_2H_6 from which HCl is difficult to remove.

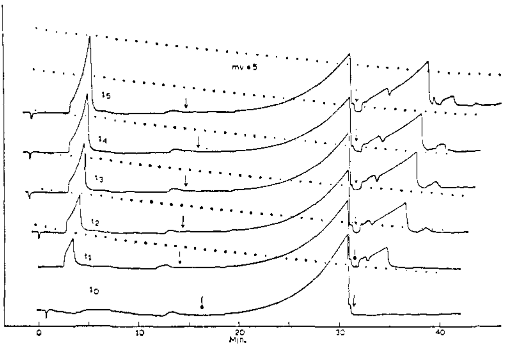

Figure 2. Analytical curves obtained on the decomposition of tetraborane(10) at 50°, 106 Torr. The curves were obtained at half-hour intervals.

The reaction flask for the kinetic studies had a volume of approximately 125 cc. It was attached to one arm of a 120° three-way stopcock. The second arm of this stopcock was sealed off, and the volume (0.532 cc) of the stub plus the hole in the stopcock plug were determined by the weight of mercury required to fill them. The third arm of the stopcock was attached to the analytical system (Figure 1) at E. This arrangement makes possible the periodic removal of samples for analysis without disturbing the course of the reaction.

The analytical system is a modification of the fractionation codistillation apparatus developed by Cady and Siegwarth[10] and used by Fehlner and Koski.[11] The procedure consisted of quickly charging the thermostated (±0.2°) reaction flask to approximately the desired pressure as indicated by the capillary manometer (M). A more accurate estimate of the initial amounts of B_4H_{10} is obtained in its initial analysis at the beginning of each run. The contents of the reaction flask were isolated and all excess B_4H_{10} returned to the storage tube. As soon as possible a sample was taken into the dosing stub and then transferred to the glass spiral (S_1). This was accomplished by pumping the contents of the stub through the spiral cooled to −196° with liquid nitrogen. The spiral was then isolated and the helium stream previously by-passing the spiral was diverted through it, and the column C kept at −196°. The liquid nitrogen bath was removed from the spiral and its contents were swept onto the column.

The column consists of $^1/_8$ in. unpacked copper tubing bent into three loops with each successive loop dipping approximately 0.5 in. deeper into the dewar flask. A copper–constantan thermocouple is soldered to the lowest loop so that the temperature at this point can be monitored during the course of the analysis. The flow of helium was adjusted to a constant flow rate of 7 cc/min in each analysis. The dewar flask around C was quickly removed, the liquid nitrogen dumped out, and the empty dewar flask replaced. As the temperature of the column rises the more volatile components, in order, are swept out of the column past the detector thermistor of the microcell D. The difference signal between the reference and detector thermistors in a bridge circuit is fed into a recorder in the usual way. Each minute during the analysis the output from the microcell is interrupted for approximately 3 sec and the output of the thermocouple is recorded. This is accomplished automatically through the use of a clock mechanism and a relay. The thermal gradient therefore appears on each of the records. Figure 2 shows a series of analyses which indicate the changes in the composition of the reaction mixture as a function of time. The time scale in the figure is approximate and represents the time required for obtaining a single analysis. The six analyses shown were done at 0.5-hr intervals so that the difference between t_0 and t_5 is 2.5 hr. The relative positions of the six records were adjusted so that they could be shown superimposed conveniently. For this reason also the ordinate is identified only by its dimension so that the records could be vertically telescoped. On any one record the full scale of the recorder was 0–12.5 mV, although the output of the cell could be as high at 250 mV for large samples. In this case the cell output was attenuated to bring it into proper range. Attenuation of cell output rather than that of the recorder range was necessary

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[9] R. Schaeffer and F. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962).

[10] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

[11] T. P .Fehlner and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 1012 (1964).

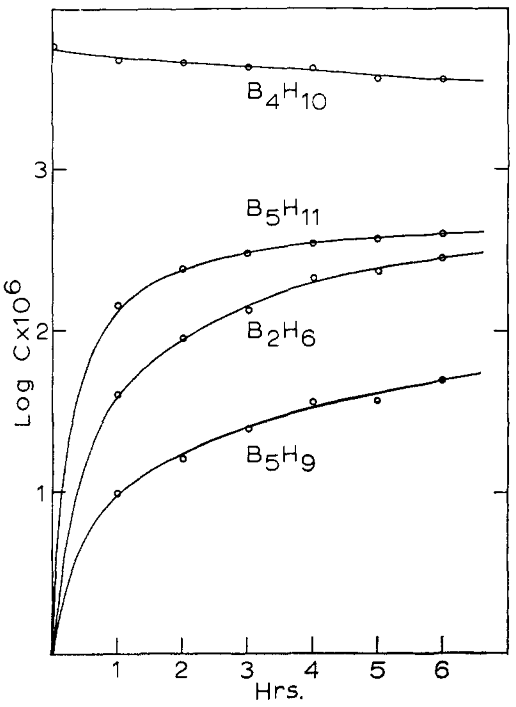

Figure 3. The composition of the mixture obtained in the decomposition of tetraborane(10) at 40° with an initial pressure of 107 Torr.

because the thermocouple required the 0–12.5 mV recorder range. Thus the portions of the curves between the arrows would have to be multiplied by five to put them on the same scale as the rest of the record. The dotted lines show the thermocouple output. The superimposed records indicate the reproducibility of the thermal gradient. The small negative spike at the beginning of each record occurs at the time at which the dewar flask around C was emptied. The peaks from left to right correspond to B_2H_6, B_4B_{10}, and a mixture of B_5H_{11} and B_5H_9. The peaks beyond these, appearing first at t_2 and becoming prominent at t_5, are due to B_6 hydrides, but their complete identification and analysis were not a part of this work.

The small feature between the B_2H_6 and B_4H_{10} peaks was identified as CH_3Cl by mass spectral analysis. This substance was present in only two of the ten runs and was apparently a contaminant in one of the B_4H_{10} preparations. Its presence does not influence the course of the B_4H_{10} decomposition.

If the time for analysis exceeds the desired kinetic time interval it is possible to hold samples for analysis in U_1, U_2, and U_3 (Figure 1) at −196°. By suitable use of the by-pass stopcocks these samples can be transferred to the column when it becomes available.

The areas of all peaks were measured with a planimeter and converted to micromoles by the use of calibration constants determined on known quantities of the pure substances. Pure components can be recovered from mixtures by diverting the helium stream from the column through the removable spiral S_2 while this substance is being recorded. The trapped product is then isolated in S_2 from which it can be removed for mass spectral or other suitable analysis. This procedure is also helpful in resolving overlapping peaks such as those obtained in recording the two pentaborane peaks. Any portion of these peaks may be trapped in S_2 and returned to S_1 for a second analysis. By examining these "sections" it is possible to reconstruct the original peak by superimposing component peaks of the pure substances.

The temperatures of first appearances of the substances that we have studied in this apparatus appear to be reproducible to ±1°. For the substances of this work, B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11}, they were −165, −112, −84, and −80°, respectively. It is clear, therefore, that even the least stable B_5H_{11} is likely to survive, with little decomposition, from the time that it is removed from the reaction mixture until its analysis is complete.

Results

The decomposition was studied at temperatures of 40, 50, and 60° and at pressures of approximately 36, 72, and 110 Torr at each of these temperatures. Figure 3 shows the principal features of the results obtained in this work. The data shown were obtained at 40° with an initial pressure of 107 Torr. The log scale on the ordinate was used so that relatively large differences in concentrations between B_4H_{10} and the other components could be displayed more compactly. After 6 hr, for example, 60% of the B_4H_{10} remains while the next most abundant component, B_5H_{11}, is present to an extent of about 10% of the B_4H_{10}. The abundance order, B_4H_{10}, B_5H_{11}, B_2H_6, and B_5H_9, respectively, was observed in all runs.

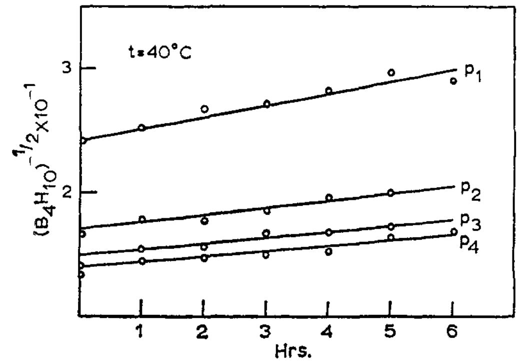

Figure 4. Plot ($^3/_2$ order) of the decomposition of tetraborane(10): P_1 = 34 Torr, P_2 = 72 Torr, P_3 = 107 Torr, and P_4 = 110 Torr are the initial pressures of B_4H_{10}.

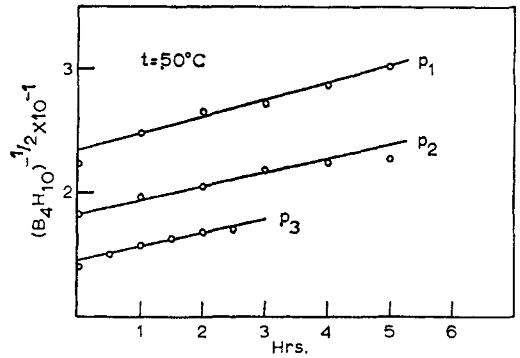

Figure 5. Plot ($^3/_2$ order) of the decomposition of tetraborane(10): P_1 = 37 Torr, P_2 = 73 Torr, and P_3 = 106 torr are the initial pressures of B_4H_{10}.

The appropriate function of the B_4H_{10} concentration was plotted for $^1/_2$, 1st, $^3/_2$, and 2nd order kinetics. Straight lines were obtained in all but two runs, only for the $^3/_2$ order plots (Figures 4, 5, and 6). There is definite curvature in the plots at 60° for the two lower pressures. This suggests a change in mechanism at higher temperature and lower pressures. When the fraction of B_4H_{10} remaining at time t was plotted against t for the two lower pressure runs at 60°, the curves were nearly identical up to the point at which 40% of the B_4H_{10} had reacted. Beyond this point the rate of disappearance of B_4H_{10} was slightly higher for the lower pressure run. This observation suggests that up to 40% decomposition the reaction is first order with respect to B_4H_{10}. Using the observed time for 40% disappearance, a first order rate constant was calculated and used in plotting the dashed lines in Figure 7. The solid curves in this figure are the plots of the experimental B_4H_{10} concentrations. The initial decomposition of B_4H_{10} at both pressures is proceeding at a rate of higher

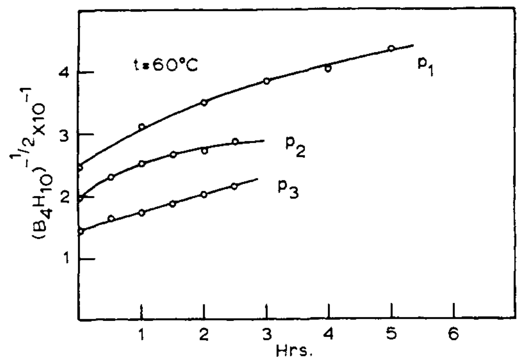

Figure 6. Plot ($^3/_2$ order) of the decomposition of tetraborane(10): P_1 = 36 Torr, P_2 = 73 Torr, and P_3 = 106 Torr are the initial pressures of B_4H_{10}.

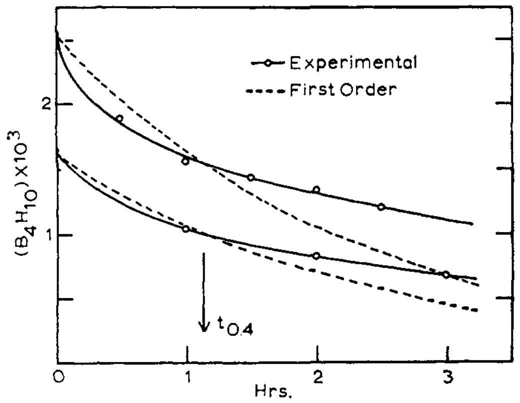

Figure 7. Comparison of the decrease in concentration of tetraborane(10) at 60° with first order decomposition, using the first order rate constants obtained for 40% decomposition. The upper curve corresponds to an initial pressure of 73 Torr and the lower one to 37 Torr.

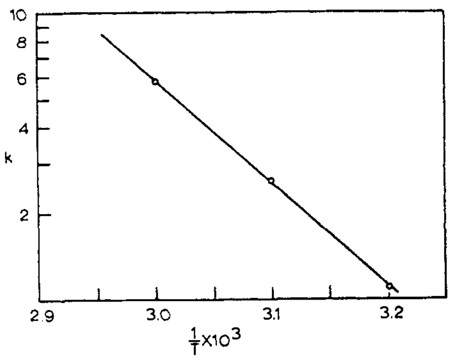

Figure 8. Arrhenius plot of the $^3/_2$ order rate constants obtained at 40, 50, and 60°.

than first order up to 40% decomposition, but the lower pressure run more nearly follows first order behavior.

The slopes of the lines in Figures 4 and 5 and of the straight line in Figure 6 were used to determine $^3/_2$ order rate constants at the three temperatures. The values obtained at 40, 50, and 60°, respectively, are 3.14 × 10^{-4}, 7.21 × 10^{-4}, and 1.61 × 10^{-3} $l.^{1/2}/mol^{1/2}$ sec. The Arrhenius plot of these values, shown in Figure 8, yields an activation energy for the overall process of 16.2 kcal/mol. The preexponential A factor is 1.4 × 10^8 $l.^{1/2}/mol^{1/2}$ sec. The raw analytical data appear in Table I.

Table I. Analytical Data

P, Torr, t, °C	Time, hr	Mol/l. × 10^4 B_4H_{10}	B_2H_6	B_5H_9	B_5H_{11}
36, 60	0	16.5	0	0	0
	1	10.3	0.925	0.645	2.90
	2	8.27	1.15	0.692	4.02
	3	6.79	1.47	0.760	4.51
	4	6.13	1.86	0.968	4.53
	5	5.25	2.05	0.969	4.53
73, 60	0	25.4	0	0	0
	0.5	19.0	1.02	0.692	1.18
	1.0	15.7	1.53	0.899	2.46
	1.5	14.3	2.11	1.11	3.20
	2.0	13.4	2.27	1.04	3.38
	2.5	12.1	2.80	1.31	4.42
106, 60	0	48.3	0	0	0
	0.5	36.8	2.01	1.61	2.93
	1.0	33.8	3.33	1.66	5.64
	1.5	29.1	4.47	1.50	5.87
	2.0	24.6	4.91	1.73	7.48
	2.5	21.8	5.94	2.07	8.69
37, 50	0	20.1	0	0	0
	1	16.4	0.359	0.171	1.13
	2	14.3	0.959	0.272	2.01
	3	13.7	1.05	0.346	2.41
	4	12.2	1.23	0.566	2.74
	5	11.1	1.53	0.692	3.21
73, 50	0	30.8	0	0	0
	1	26.9	1.05	0.553	2.07
	2	24.1	2.01	0.784	3.46
	3	21.6	2.33	0.968	3.65
	4	19.9	3.14	0.254	3.99
	5	19.4	3.61	0.667	4.70
106, 50	0	52.5	0	0	0
	0.5	44.7	1.26	0.276	1.38
	1.0	40.4	1.68	0.415	2.80
	1.5	38.4	2.29	0.600	3.91
	2.0	35.2	2.99	0.760	4.21
	2.5	35.7	4.10	1.29	4.72
34, 40	0	17.8	0	0	0
	1	16.1	0	0	0
	2	14.0	0	0.055	0.335
	3	13.7	0.210	0.099	0.641
	4	12.5	0.210	0.099	0.878
	5	11.4	0.269	0.124	0.938
	6	12.0	0.572	0.197	1.23
72, 40	0	36.3	0	0	0
	1	31.8	0.179	0.124	0.654
	2	32.1	0.555	0.147	1.55
	3	29.5	0.778	0.197	1.85
	4	26.1	0.993	0.222	1.96
	5	25.2	1.44	0.273	2.39
107, 40	0	59.0	0	0	0
	1	47.8	0.402	0.099	1.48
	2	46.8	0.914	0.161	2.48
	3	44.0	1.36	0.246	3.08
	4	43.4	2.12	0.370	3.46
	5	37.4	2.37	0.370	3.70
	6	37.9	2.82	0.493	4.08
110, 40	0	52.3	0	0	0
	1	41.4	0.436	0.147	1.10
	2	41.5	1.03	0.173	2.46
	3	36.5	1.44	0.199	2.61
	4	36.3	1.77	0.223	2.67
	5	34.8	2.05	0.320	3.23

Discussion

The facts that other studies above 60° gave first order kinetics, one study[12] at 20° and all except two of our runs yielded $^3/_2$ order, suggest that these two runs might be interpreted in terms of mixed $^3/_2$, first order processes. Using the $^3/_2$ order k_2 found in the 60°, 106 Torr run, and the integrated mixed order equation

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(12) See p 75 in ref 5.

$\log [C^{1/2}/(k_1 + k_2C^{1/2})] = -k_1t/2 + \log [C_0^{1/2}/(k_1 + k_2C_0^{1/2})]$, nearly parallel straight lines were obtained when the left member of the above equation was plotted against t. From the slopes of these plots an average first order constant, $k_1 = 1.59 \times 10^{-5}$ sec^{-1}, was obtained. The first order constant obtained by Pearson and Edwards at 60° was 1.8×10^{-5} sec^{-1}. At pressures under 100 Torr, 60° appears to represent the temperature below which $^3/_2$ order kinetics is predominant, while first order is observed above this temperature.

When $\log (C_0/C)$ of B_4H_{10} is plotted against the concentration of B_2H_6 a straight line is obtained in each run. Assuming that the rate of production of B_2H_6 is $^1/_2$ order ($d[B_2H_6]/dt = k'[B_4H_{10}]^{1/2}$) with respect to B_4H_{10}, and that the rate of disappearance of B_4H_{10} is $^3/_2$ order, it is possible to eliminate time from the two differential equations and obtain an integrated equation, $\log (C_0/C) = (k_2/k')[B_2H_6]$, where C_0 is the initial concentration of B_4H_{10}, C is the concentration of B_4H_{10} when the concentration of diborane = $[B_2H_6]$, and k' is the constant for the $^1/_2$ order process. Plots of the left member of this equation against the B_2H_6 concentration should yield the same straight line for all runs at the same temperature. The small amount of B_2H_6 produced in the 40° runs made reliable checking of the constancy of k' impossible. The scatter of points at each pressure, however, seemed to center around a common line. Excellent straight lines were obtained for all other runs and for the previously mentioned run at 20°. A single straight line was obtained for the 50° runs at 73 and 106 Torr, but the 37-Torr run at this temperature gave a straight line with a larger slope, indicating a smaller k'. The 60° plots produced three straight lines whose slopes increased with decreasing pressure, indicating an increase in k' with increasing pressure. The variation of k' with temperature at constant pressure, on the other hand, shows a decrease with increasing temperature. The observed pressure and temperature dependence of k' indicate that the source of the B_2H_6 may be an activated complex which decomposes by two paths, and that B_2H_6 is not consumed in any reaction.

$$\begin{tikzcd} A^* \arrow[r, "1"] \arrow[d, "2"] & B_2H_6 \\ \text{other products} & \end{tikzcd}$$

Path 1 requires molecular collisions for deactivation while path 2 is a spontaneous unimolecular process with the probability of occurrence increasing with increasing temperature. The two coincident lines obtained for the 50° runs at the higher pressures also suggest that there exists a saturation pressure at each temperature above which the first path becomes the controlling factor. The determination of such saturation pressures is planned for future work.

Nonvolatile solid products were obtained almost immediately in all runs, but there was no evidence for the production of the volatile solid $B_{10}H_{14}$. The solid settled only on the horizontal portions of the reaction flask, leaving vertical sections clear. The solid product therefore must arise through the rapid polymerization of low molecular weight fragments in the gas phase. The fraction of boron in B_4H_{10} going to solid increases and the fraction going to pentaboranes decreases with decreasing temperature. Thus the formation of solid and of the pentaboranes may arise from the same intermediate which may react in the manner shown in eq 1 and 2. One could then assume that the importance of

$$\begin{array}{l} B_2H_4 \longrightarrow B_2H_2 + H_2 \\ \qquad\qquad\quad \hookrightarrow (BH)_x \end{array} \qquad (1)$$

$$B_2H_4 + B_3H_7 \longrightarrow B_5H_{11} \qquad (2)$$

the second reaction increases with temperature.

There is also an increase with temperature in the fraction of the boron in B_4H_{10} going to B_2H_6 so that, in general, the fraction of boron in B_4H_{10} going to volatile products increases with temperature.

Some hexaboranes were produced at the higher pressure runs at 40 and 50°, but not in the 60° runs, even at the highest pressure. The hexaboranes may therefore result from the bimolecular collision of a fragment such as B_3H_7, which is important only at higher pressures and at temperatures at which B_3H_7 may survive for a sufficient time.

The complexity of the tetraborane(10) decomposition suggests a chain mechanism in which the initiation step is a first order process which becomes rate controlling when the chain length is small. The gross observations can then be interpreted in terms of the possible effects of temperature and pressure on chain length. A complete understanding will be possible after more data become available not only on this system but also on the components of this system. The following sequence of reactions leads to a rate equation which is the sum of a first and $^3/_2$ order process in B_4H_{10}.

$$B_4H_{10} \xrightarrow{1} B_3H_7 + BH_3$$

$$B_3H_7 \xrightarrow{2} BH_2 + B_2H_5$$

$$B_2H_5 \xrightarrow{3} BH_2 + BH_3$$

$$BH_2 + B_4H_{10} \xrightarrow{4} B_4H_9 + BH_3$$

$$B_4H_9 \xrightarrow{5} B_2H_5 + B_2H_4$$

$$B_2H_4 \xrightarrow{6} \text{solid} + H_2$$

$$2BH_2 \xrightarrow{7} B_2H_4$$

$$2BH_3 \xrightarrow{8} B_2H_6$$

Applying the steady state hypothesis to BH_2, BH_3, B_2H_5, B_3H_7, B_4H_9, and B_2H_4, one obtains the following expression for the rate of disappearance of B_4H_{10}

$$-R(B_4H_{10}) = k_1[B_4H_{10}] + k_1^{1/2}k_4/k_7^{1/2}([B_4H_{10}]^{3/2})$$

The B_5H_9 produced in our systems we believe comes primarily from the decomposition of B_5H_{11}. The previously suggested route to B_5H_{11} production removes chain-propagating fragments in greater proportion at higher temperature, in agreement with the observed tendency to first order kinetics at higher temperatures.

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