A Kinetic Study of the Gas-phase Thermolysis of Hexaborane(10) *

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The gas-phase thermolysis of B_6H_{10} has been studied kinetically by mass spectrometry for pressures in the range 1—7 mmHg, and at temperatures between 75 and 165 °C (348—438 K). Hexaborane(10) was found to decompose by a second-order process with an activation energy of 79.7 ± 3.7 kJ mol^{-1}. The rate of decomposition is much slower than implied by qualitative statements in the literature. The main products are hydrogen and a non-volatile solid. The initial rates of hydrogen production and B_6H_{10} consumption are in a ratio of 1 : 1, but the final amount of hydrogen produced is nearer twice that of the B_6H_{10} consumed; added hydrogen has little effect on the initial rates. The simplest mechanism consistent with these observations involves an initial bimolecular rate-controlling step, with rapid elimination of two molecules of hydrogen from the $(B_{12}H_{20})^\ddagger$ activated complex to give $\{B_{12}H_{16}\}$, a previously unconsidered reactive intermediate, which is immediately removed as a solid by condensation polymerization. Other modes of decomposition of the activated complex, although less likely as routes to the solid, do provide a plausible explanation for the minor amounts of B_5H_9 and $B_{10}H_{14}$ that are produced. A B_{12} species is observed in the mass spectrum, but this is shown to be a secondary-process ion resulting from an ion–molecule reaction in the source of the mass spectrometer.

The mechanisms of thermal decomposition of B_2H_6 and the ensuing thermolytic interconversion reactions of the higher hydrides are of central importance in the field of boron hydride chemistry.[1,2] A particularly intriguing aspect is the virtual absence of hexaboranes and other species intermediate between the pentaboranes and $B_{10}H_{14}$ in this complex interacting system. Schaeffer[3] has suggested that the Lewis-base properties of B_6H_{10}, as revealed in its recent chemistry,[4—7] provide a likely explanation for this apparent anomaly, and has further suggested that this borane may play a crucial role in the pyrolysis process by virtue of its propensity to react with acidic borane intermediates such as $\{BH_3\}$, $\{B_3H_7\}$, $\{B_4H_8\}$, B_8H_{12}, and $\{B_9H_{13}\}$.

Surprisingly little work has been done on B_6H_{10}, and none of it is of a kinetic nature. The early experiments of Stock[8] and the more recent pyrolysis studies of Schaeffer and co-workers[6] were carried out mainly on liquid samples, and the results may not therefore be directly relevant to events in the gas phase. Some preliminary gas-phase work was reported from this laboratory[9] but the sample used is now known to have been impure.

To assess the role of B_6H_{10} in the thermolysis of B_2H_6 we are carrying out a systematic study of cothermolysis reactions of B_6H_{10} with other boranes in the gas phase. As a precursor to this we have made a detailed kinetic study of the thermolysis of pure B_6H_{10}, the results of which form the subject of this paper. A notable feature of the work is that *all* the volatile components of the reacting mixture, including hydrogen, have been analysed quantitatively and continuously. This has involved considerable modification of the original mass-spectrometric method described in the earlier reports from this laboratory, and has resulted in the development of a technique for viscous-flow sampling which, to the best of our knowledge, has not been previously described.

Experimental

Materials.—The boranes B_2H_6 and B_6H_{10} were prepared by methods described in the literature,[10,11] and purified by standard grease-free vacuum-line techniques. Pentaborane(9) was provided by courtesy of Dr. R. E. Williams, Chemical Systems Inc., California, and $B_{10}H_{14}$ was a commercial sample (Olin Chemicals Co. Ltd.), sublimed before use. CP Grade hydrogen and helium, Standard Grade argon, and Research Grade krypton were obtained from BOC Ltd.; all were used without further purification.

Instrumentation.—The progress of each reaction was followed by two mass spectrometers: a Kratos MS30 double-beam instrument to monitor the boranes, and a smaller MS10S to analyse quantitatively for dihydrogen. The MS30 was equipped with a DS55 data-acquisition system consisting of a NOVA 3 minicomputer coupled with a Phoenix Disk Drive, model 6050. Operation was through a Hewlett Packard HP2623A graphics terminal. The NOVA 3 was linked by direct line to the University's central computer (Amdahl VM/470) which houses the suite of programs used in the data analysis. The MS30 was operated at its lowest resolution (*R ca.* 1 000) throughout and was scanned at a rate of 10 s per decade. Unless otherwise stated the source conditions were as follows: ionizing electron beam 70 eV, accelerating voltage 4 kV, trap current 300 μA, temperature *ca.* 80 °C with cooling by a constant pressure of compressed air, and pressure-gauge reading 5×10^{-8} to 1×10^{-6} mmHg. Routine data collection was performed under the control of the DS55 low-resolution software using the peak at *m/z* 40 from argon as an internal lock-mass; the spectrometer was calibrated against the spectrum of perfluorokerosene (pfk). The B_{12} ion–molecule study was carried out in double-beam mode, with pfk as calibrant in the second beam.

The MS10S was used with its standard collector slit (width 0.25 mm) and preamplifier unit (input resistance 10^{11} Ω). It was operated in its manual mode and output was taken to a Linseis type LS4 chart recorder. To prevent excessive backstreaming (which led to an unacceptable signal-to-noise ratio with dihydrogen) the original diffusion pump was replaced with an Edwards Diffstak pumping unit working at an optimized pumping speed of 10^{-2} m^3 s^{-1}.

Temperature control of the oven containing the reaction vessel was achieved with an Oxford Instrument's digital temperature controller, model DTC-2, fitted with an external high-power output unit, type OP.3KW. This was used in conjunction with a 100-ohm platinum resistance sensor and the appropriate Range Card, type CP07. Temperature homo-

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* Throughout this paper braces {} are used to denote non-isolable reactive species.

Non-S.I. units employed: eV ≈ 1.60×10^{-19} J; mmHg ≈ 133 Pa.

geneity over the surface of the reaction vessel was monitored by several patch thermocouples, type KPSA-K/1 from Comark Electronics Ltd., and found to be within ±1°; temperature stability was better than ±0.5 K.

Mass-spectrometric Methods of Analysis.—Development of a novel viscous-flow sampling method. The methods of analysis used in this work have developed out of the earlier efforts in this laboratory to devise a technique for the continuous sampling of boranes in borane–hydrogen mixtures.[9] However, the need to obtain reliable quantitative data from which precise kinetic parameters can be determined has necessitated a fundamental reappraisal of the method of sampling and calibration. It can be shown by a detailed consideration of the (predominantly viscous) flow through the sampling capillaries that the procedure adopted in the earlier exploratory work, of using the response of one gas (*i.e.* argon) in the mixture to correct the response of another, is likely to cause an automatic error in the calculated response of the second gas. Moreover, the effects are likely to be exacerbated in reactions in which dihydrogen is produced, because of its low viscosity and molecular weight.

Ideally, a method of sampling was required in which the components of the mixture would flow independently of one another, such that the calibration curves of total ion current *vs.* partial pressure for the individual boranes would remain invariant to changes in the mixture. We therefore explored, in some detail, batch sampling methods employing molecular flow through the capillaries, but these proved unsuccessful because of insurmountable problems associated with adsorption of the boranes on the walls of the sampling reservoir and other parts of the system at the low pressures required (*ca.* 10^{-2} mmHg).

Being obliged to resort to viscous flow, we sought other means of ensuring that the calibration curves would be unaffected by changes in the composition of the mixture. We achieved this by including a large background pressure of an inert gas in each mixture, both in the calibration procedure and in the actual thermolysis experiments. The purpose of this added gas is to reduce the variability in viscosity and the effects due to changes in the total pressure in the reaction mixture to a level which is negligible compared with other probable experimental errors. Helium, which has a low efficiency as a kinetic third body, was chosen for this purpose, and pressures of *ca.* 100 mmHg were found to be adequate. A feature of this method is that the rate of flow of any particular component through the sampling capillaries, and therefore the response of the spectrometer to that component, is predicted (for the relatively low partial pressures of 0—10 mmHg employed in this work) to be approximately linearly related to its partial pressure in the mixture, and this expectation is realized in practice in the new calibration curves.

Calibration procedure and data analysis. Two types of information are required in order to analyse the spectrum of a mixture: (*a*) calibrations of spectrometer response *versus* partial pressure in the reaction vessel for each component; (*b*) mass-spectral profiles, under standard source conditions, for each borane. A known partial pressure of argon was included in each calibration and reaction mixture to act as a standard, so that correction could be made for changes in spectrometer performance and sensitivity. The argon calibration curve was obtained by recording the ion current of the peak at *m*/*z* 40 as a function of argon partial pressure, for a series of mixtures of argon in a fixed pressure (100 mmHg) of helium at room temperature. Some calibrations were also recorded at higher temperature and found to be in agreement with the room-temperature data. As a general procedure, each mixture was scanned repetitively and the average of 5—10 scans was taken when the response became stable. The calibration curve for a particular borane was obtained similarly by noting the individual total ion currents for borane and argon in a series of mixtures (covering a range of partial pressures) of that borane together with fixed amounts of helium (100 mmHg) and argon (5 mmHg). The argon normalization factor applied to the borane response for each mixture, both in the calibration procedure and in the actual thermolysis experiments, was taken as the ratio of the argon response expected from its calibration curve to the argon response observed in the mixture. In the thermolyses there were frequently small discrepancies between the computed and actual pressures of B_6H_{10} at time $t = 0$. These were attributed to unavoidable mass-discrimination effects, * and in such cases the pressures were further normalized so that the extrapolated values at time $t = 0$ (determined in this particular study from plots of the reciprocal pressure *versus* time) corresponded exactly with the partial pressure of B_6H_{10} known to be present in the reaction vessel. Evidence that this approach is justified is seen later in Figure 5 which shows data for three runs at 426 K (see also Table 2), with the same initial pressure of B_6H_{10}, to be accurately superimposable after being treated in this way.

Throughout this work care was necessary to ensure thorough mixing of all components of a gas mixture, and subsequently to prevent demixing when transferring the sample by expansion from one vessel to another. Special precautions were necessary with $B_{10}H_{14}$ because of its low volatility and general reluctance to diffuse against a background pressure of another gas, particularly when in a confined space. The calibration data were finally obtained by use of a specially designed reaction vessel which facilitated quantitative sublimation of a known weight of $B_{10}H_{14}$ from a removable sidearm, followed by complete vaporization in the inert gas mixture. Care was taken not to exceed the reported vapour pressure of $B_{10}H_{14}$ at the temperature used (393 K), although information in the literature on this subject is confusing.[14—16]

New standard spectra were recorded for B_2H_6, B_5H_9, B_6H_{10}, and $B_{10}H_{14}$ under the modified conditions. There were no gross differences from those reported in ref. 9, except for B_6H_{10} itself. The spectrum recorded in the present work agrees with that given by Gibbins and Shapiro[17] for pure B_6H_{10}, and it was concluded that the sample used in ref. 9 contained an impurity of *ca.* 10% B_5H_{11}.

The calibration data and standard spectra were all converted into forms suitable for incorporation into a least-squares curve-fitting program, details of which have already been given.[9] The programs have been altered to suit the requirements of the modified experimental method.

Analysis of hydrogen. The development of a means of measuring dihydrogen quantitatively and continuously, in parallel with the boranes in these mixtures, is a major feature of this work. This has been achieved by introducing an additional capillary leak from the reaction vessel to a second dedicated mass spectrometer. The capillary was connected to the MS10S by

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* Changes in overall response of the spectrometer are inevitable when studying boranes, because of the deleterious effect which these materials have on the source. Inclusion of argon as an internal calibrant is only effective in dealing with this problem if changes in response are uniform across the mass range. However, this is frequently not the case, and such mass-discrimination effects have long proved troublesome in attempts to use mass spectrometry as a quantitative analytical tool.[12] In concurrent work[13] we have alleviated such problems by conditioning the source with a sample of the original mixture both prior to a run and in between individual measurements. We have also found it useful to include krypton, which has a base peak at *m*/*z* 84, as a second marker along with argon to indicate the extent of any non-uniform changes in response *during* a run, and thereby provide a criterion for rejecting potentially unreliable data. Both of these developments have been incorporated to advantage in the work described here.

glass tubing of internal diameter 8 mm and length 11 m. A helical trap of total length 6.6 m was included in this line to remove boranes, thereby ensuring that the signal at *m*/*z* 2 contained no contribution from hydrogen ions produced by borane fragmentation. This procedure also avoided contamination of the MS10S source and resulted in remarkably stable operating conditions and greatly extended source lifetime. The trap is capable of removing even B_2H_6, despite the fact that this borane has a bulk vapour pressure of *ca.* 10^{-4} mmHg at the temperature of liquid nitrogen. This is presumably due to cryoadsorption on the walls of the glass spiral, and care had to be taken to ensure that excessive quantities of condensed material did not accumulate, otherwise the bulk vapour pressure was eventually established and the borane passed through.

The arguments presented earlier concerning flow in the capillaries are generally applicable to the analysis of boranes with the MS30 and hydrogen with the MS10S. The calibration procedure for hydrogen was essentially the same as that for the boranes, except that the constant background of helium was used as the internal calibrant for the hydrogen analysis.

Thermolysis Procedure.—The gas mixtures were prepared in calibrated bulbs on a high-vacuum line fitted with HP Rotoflo greaseless taps. Pressure measurement was by mercury manometer. The mixtures were then expanded slowly into a conditioned Pyrex reaction vessel (volume *ca.* 1 dm^3) enclosed in a thermostatted oven at the required temperature, and this was taken as the zero reaction time. Samples were admitted without delay into the two mass spectrometers *via* separate 180-mm lengths of 0.1-mm diameter Veridia tubing, and scanning was initiated immediately. Approximately 1 min later the reaction vessel was isolated from the vacuum line by means of a long-distance-control, greaseless tap (Youngs Scientific Glassware Ltd.), the handle of which protruded through the base of the insulated oven. A similar tap, with a capillary sidearm to reduce dead-space, allowed the flow of sample to the mass spectrometer to be interrupted, so that slow reactions could be monitored periodically rather than continuously. In some of the later experiments source-conditioning procedures were carried out as indicated in the footnote on p. 542.

Results and Discussion

Main Features.—Pure B_6H_{10} was found to be surprisingly stable in the gas phase. At a pressure of 3.5 mmHg no significant decomposition was detected over a period of 24 h at 348 K. A previous study[9] on a sample now known to have been impure (see Experimental section) had indicated extensive decomposition under similar conditions, to give B_2H_6 as the major product. At 393 K the pure sample decomposed slowly to yield mainly hydrogen, together with very small amounts of B_5H_9 and $B_{10}H_{14}$ in an approximate molar ratio of 5:1 as the only stable volatile products; B_2H_6 was detected only in trace amounts and did *not* accumulate. Most of the boron (*ca.* 90%) disappeared entirely from the gas phase and was deposited predominantly on the lower walls of the vessel as a yellowish solid hydride. At higher temperatures there was no significant change in the product distribution but the faster rate of reaction resulted in more stable operating conditions and a consequent improvement in the quality of the borane data. A typical reaction profile at 426 K is shown in Figure 1.

In the early stages of thermolyses at lower temperatures (*e.g.* 373 K) weak borane-like peaks were seen in the mass spectrum in the region *m*/*z* 90—100, with a base peak at *m*/*z* 93, indicative[18] of B_8H_{12}. The intensity of these peaks decreased as the reaction proceeded and they were eventually lost under the B_8 and B_9 envelopes of the fragmenting $B_{10}H_{14}$. Later in the reaction B_{13}, B_{14}, and B_{15} species were observed, although at barely detectable levels. In an experiment at 333 K designed to look specifically for reactive intermediates in the early stages of the decomposition, a sample of B_6H_{10} was held at a much higher pressure (23.2 mmHg) and monitored at very high gain on the mass spectrometer. Under these conditions peaks in the region *m*/*z* 100—110, characteristic[18] of B_9H_{15}, were also observed, at one stage in greater intensity than those in the B_8 region. An interesting B_{12} species was also detected, but this was subsequently shown to be the result of an ion–molecule reaction in the source of the mass spectrometer.

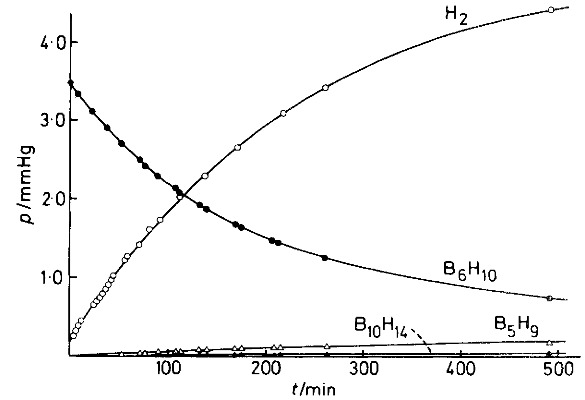

Figure 1. Reaction profile for thermolysis of B_6H_{10} (p_0 = 3.51 mmHg) at 426 K

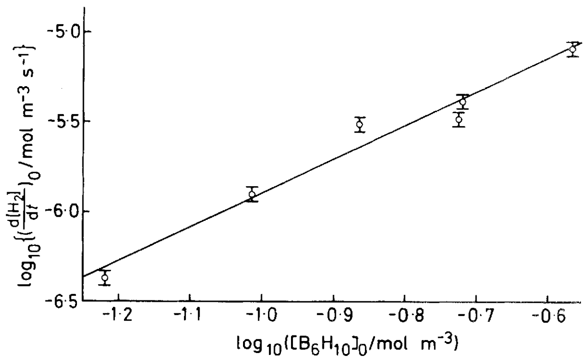

Figure 2. Plot of the log of the initial rate of hydrogen production *versus* the log of the initial concentration of B_6H_{10}, showing the reaction to be second order. Slope = 1.89 ± 0.17

The Order of the Reaction.—The rate-determining step was shown to be a homogeneous gas-phase reaction by establishing that the rates of B_6H_{10} consumption and of H_2 formation were no greater in a conditioned packed reaction vessel than in an unpacked vessel, despite a 33-fold increase in surface-to-volume ratio. Attempts to deduce the order of the reaction, based on integration (order-plot) methods, were inconclusive because in general the borane data were not sufficiently precise to distinguish unambiguously between the various possibilities. Moreover, the (more precise) hydrogen data could not be used for this purpose because of complications arising as a result of hydrogen being produced not only in the primary gas-phase reaction but also by decomposition of the deposited solid. To avoid such problems, the order was investigated by a study (at 393 K) of the initial rates of hydrogen production and B_6H_{10} consumption as a function of initial concentration of B_6H_{10} for pressures of 1.5, 2.4, 3.4, 4.6, 4.7, and 6.7 mmHg. The results are summarized in Table 1 and Figure 2. The latter shows a plot of the log of the initial rate of hydrogen production *versus* the log of the initial concentration of B_6H_{10}: the gradient of 1.89 ± 0.17 indicates that the production of hydrogen is second order with respect to $[B_6H_{10}]$. The borane data at 393 K follow the same straight line (although with greater scatter) consistent with the consumption of B_6H_{10} also being second order. This conclusion was confirmed from the more precise borane data obtainable at higher temperatures. For example Figure 3 shows that the second-order plot of the B_6H_{10} data in Figure 1 is linear over at least two half-lives, whereas the first-order plot is clearly curved. The consumption of B_6H_{10} therefore remains second order as the reaction proceeds, implying that there is no significant interference from products, including hydrogen. An additional experiment was carried out at 426 K in which hydrogen at a pressure of 25 mmHg was added to the initial charge of B_6H_{10}. The second-order rate constants for the initial production of hydrogen and consumption of B_6H_{10} were found to be 78 × 10^{-5} and 68 × 10^{-5} m^3 mol^{-1} s^{-1}, respectively, in good agreement with the values recorded in Table 2 (see next section) for runs carried out at 426 K with no added hydrogen.

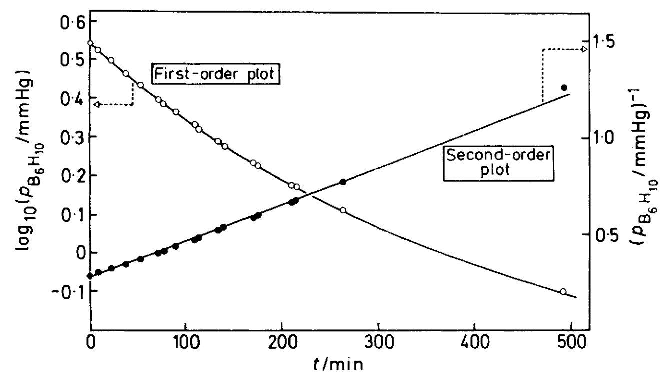

Figure 3. First- and second-order plots for the thermolysis shown in Figure 1

Table 1. Kinetic data for thermolysis of B_6H_{10} at 393 K

$10^3[B_6H_{10}]_0$[a] /mol m^{-3}	$10^7\left(\frac{d[H_2]}{dt}\right)_0^b$/mol m^{-3} s^{-1}	$10^5k_{H_2}$[c]/m^3 mol^{-1} s^{-1}
60 ± 1	4.3 ± 0.4	11.9
97 ± 2	12.5 ± 1.0	13.3
137 ± 3	30.6 ± 3.0	16.3
188 ± 4	33.0 ± 3.0	9.3
191 ± 4	42.1 ± 7.0	11.5
273 ± 5	84.1 ± 8.0	11.3
		mean 12.3 ± 2.2

[a] Initial concentration of B_6H_{10}. [b] Initial rate of hydrogen production. [c] Second-order rate constant for the initial production of hydrogen (see footnote on p. 545).

The possibility that the reaction was not second order but was, in fact, first order in the low-pressure 'pseudo-second-order' region was considered but rejected for the following reasons. (*a*) The apparent order was independent of pressure, at least over the limited range studied (1—7 mmHg B_6H_{10}), and was very close to 2.0 rather than some value between 1 and 2. (*b*) The reaction was carried out in a pressure range well above that expected for the 'fall-off' region of a molecule as complex as B_6H_{10}; moreover, the reaction was always carried out in the presence of a large excess of inert gases, He (100 mmHg), Ar (5 mmHg), and Kr (5 mmHg), which would also ensure adequate deactivation of the excited B_6H_{10} molecules and reveal palpable first-order kinetics if this were indeed the case.

Activation Energy.—The activation energy was determined by studying the temperature dependence of the observed

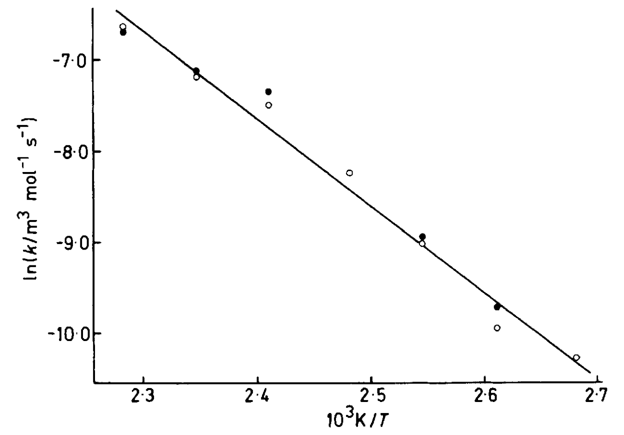

Figure 4. Arrhenius plot for the thermolysis of B_6H_{10} at constant concentration (0.134 mol m^{-3}). Open circles refer to the hydrogen data and filled circles to the borane data. The line drawn through the data represents the best fit to the hydrogen data; and that of best fit to the borane data is virtually coincident with this

Table 2. Arrhenius data for thermolysis of B_6H_{10} at constant concentration[a]

	T/K	$10^5k_{H_2}$[b]/m^3 mol^{-1} s^{-1}	$10^5k_{B_6H_{10}}$[c]/m^3 mol^{-1} s^{-1}	$k_{H_2}/k_{B_6H_{10}}$
	373 ± 1	3.48 ± 0.17	—	—
	383 ± 1	4.76 ± 0.24	6.1 ± 1.3	0.78
	393 ± 1	12.3 ± 2.1	13.2 ± 5.1	0.93
	403 ± 1	26.5 ± 1.3	—	—
	415 ± 1	55.5 ± 3.0	64.5 ± 10	0.86
(i)	426 ± 1[d]	77.6 ± 4.0	85.5 ± 9.0	0.91
(ii)	426 ± 1[d]	78.2 ± 4.0	75.7 ± 8.0	1.03
(iii)	426 ± 1	73.0 ± 4.0	83.7 ± 8.0	0.87
	438 ± 1[d]	132.1 ± 7.0	127.5 ± 13.0	1.04
			mean	0.92 ± 0.09

[a] $[B_6H_{10}]_0$ = 0.134 ± 0.003 mol m^{-3} except at 393 K. The values at this temperature are averages derived from data for thermolyses referred to in Table 1. [b] See footnote *c* in Table 1. [c] Second-order rate constant for consumption of B_6H_{10}. For greater accuracy, the rate constants were determined from the slopes of plots of the reciprocal pressure *versus* time, rather than from the initial rates, because the consumption of B_6H_{10} remained second order throughout. See also footnote on p. 545. [d] Krypton included as an additional calibrant (see Experimental section).

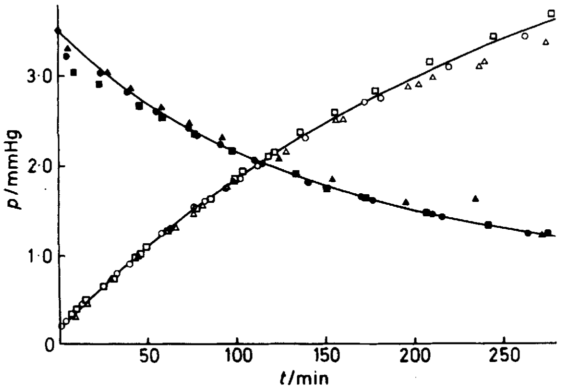

Figure 5. Reaction profiles for three separate thermolyses at 426 K and initial B_6H_{10} pressure of 3.51 mmHg. The filled circles, triangles, and squares refer, respectively, to the B_6H_{10} data from runs (i)—(iii) in Table 2, the open symbols to the corresponding hydrogen data

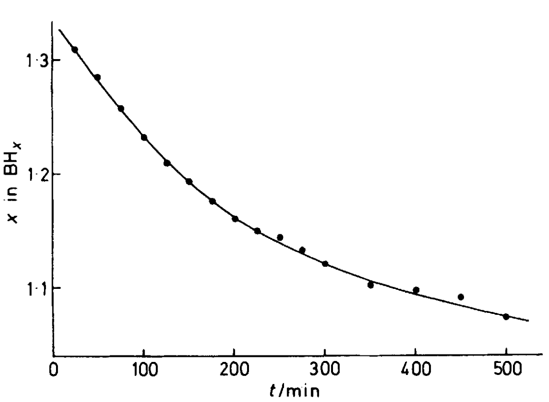

Figure 6. Variation with time of the average composition of the BH_x solid in the thermolysis of B_6H_{10} at 426 K. Values for the pressures of H_2, B_5H_9, B_6H_{10}, and $B_{10}H_{14}$ used in the calculations were taken from the smooth curves drawn through the data points in Figure 1

second-order rate constants* for hydrogen production and B_6H_{10} consumption over the temperature range 373—438 K. The results are summarized in Table 2 and presented in the form of an Arrhenius plot in Figure 4. The least-squares best fit to the hydrogen data yields a value of 79.7 ± 3.7 kJ mol^{-1} for the activation energy, and a value of $A_{obs.} = e^{15\cdot4 \pm 1\cdot1}$ (*ca.* 4.7 × 10^6) m^3 mol^{-1} s^{-1} for the pre-exponential factor. The borane data give corresponding values of 77.9 ± 5.5 kJ mol^{-1} and $A_{obs.} = e^{14\cdot9 \pm 1\cdot5}$ (*ca.* 2.9 × 10^6) m^3 mol^{-1} s^{-1}, respectively. These values for the pre-exponential factor are seen to be somewhat lower than the value of *ca.* 10^8 m^3 mol^{-1} s^{-1} predicted from transition-state theory for the bimolecular reaction of two hard-sphere molecules.[20]

Reaction Stoicheiometry.—The data in Table 2 and Figure 4 show clearly that within experimental error the initial rates of hydrogen production and B_6H_{10} consumption are in a ratio of

Table 3. Accurate masses of $B_{12}H_x^+$ fragments from low-resolution double-beam measurements*

Observed mass	Fragment	Calculated mass	Error (calc. − obs.)
141.1859	$^{10}B_0{}^{11}B_{12}H_9$	141.1821	−0.0038
140.1758	$^{10}B_0{}^{11}B_{12}H_8$	140.1743	−0.0015
139.1785	$^{10}B_1{}^{11}B_{11}H_8$	139.1779	−0.0006
138.1812	$^{10}B_2{}^{11}B_{10}H_8$	138.1815	+0.0003
137.1835	$^{10}B_3{}^{11}B_9H_8$	137.1852	+0.0017
136.1794	$^{10}B_2{}^{11}B_{10}H_6$	136.1659	−0.0135
	$^{10}B_3{}^{11}B_9H_7$	136.1773	−0.0021
	$^{10}B_4{}^{11}B_8H_8$	136.1887	+0.0093
135.1798	$^{10}B_3{}^{11}B_9H_6$	135.1694	−0.0104
	$^{10}B_4{}^{11}B_8H_7$	135.1809	+0.0011
	$^{10}B_5{}^{11}B_7H_8$	135.1923	+0.0125
134.1767	$^{10}B_4{}^{11}B_8H_6$	134.1730	−0.0037
	$^{10}B_5{}^{11}B_7H_7$	134.1844	+0.0077
	$^{10}B_6{}^{11}B_6H_8$	134.1959	+0.0192

* In these measurements the centroids of the composite peaks were determined accurately to *ca.* ±0.0010, but the resolution was not sufficient to allow multiplets at a given mass number to be distinguished. The peaks were too weak to be observed under high resolution.

1:1. The average of all values listed for the ratio $k_{H_2}/k_{B_6H_{10}}$ is 0.92 ± 0.09, and the average for the more precise data at the higher temperatures (426 and 438 K) is 0.96 ± 0.07. The data for the three runs at 426 K are reproduced in a composite reaction profile in Figure 5 to emphasize the quality and reproducibility that establish this important experimental fact.

It is also apparent from Figure 5, and more clearly from Figure 1, that the overall stoicheiometry is *time-dependent*: whereas the initial ratio is 1:1, by the end of the reaction the ratio of hydrogen produced to B_6H_{10} consumed is approximately 2. This result, in conjunction with the earlier observation that the reaction involving B_6H_{10} in the gas phase is essentially *time-independent*, implies that the change in stoicheiometry results from gradual dehydrogenation of the BH_x solid. This is put on a more quantitative basis in Figure 6 which shows the results of material-balance calculations to determine the average stoicheiometry of the BH_x solid as a function of time. The analysis indicates that the initial solid of composition $BH_{1\cdot33}$ readily loses hydrogen under thermolysis conditions, eventually yielding a material BH_x having x *ca.* 1.0.

The B_{12} *Ion Molecule.*—Mass spectra recorded under very high gain revealed a borane-like profile with a cut-off at m/z 140, some three orders of magnitude less intense than the main B_6 signal. The feature was detected during a thermolysis run, but was shown later to be present even when purified B_6H_{10} was maintained at room temperature. The shape of the main B_{12} profile was unusual for a borane in that the base peak (m/z 138) was only two mass units less than the cut-off. Closer examination revealed that the profile matched very closely that expected for a $B_{12}H_8^+$ species with the normal distribution of boron isotopes, and this was consistent with accurate mass measurements which also suggested that the profile was dominated by isotopomers from the species $B_{12}H_8^+$ (see Table 3), with only a minor contribution from fragments with a different number of hydrogen atoms.

A careful study was made of the B_{12}/B_6 intensity ratio as a function of the ion-source pressure, utilizing three different capillary leaks to provide three different source pressures for each of a series of reaction-vessel pressures. The results reveal a linear increase in the B_{12}/B_6 intensity ratio with increasing source pressure, indicative[21—23] of ion–molecule formation. The

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* The second-order rate constants referred to here and in Tables 1 and 2 were evaluated from the expressions $d[H_2]_0/dt = k_{H_2}[B_6H_{10}]_0^2$ and $-d[B_6H_{10}]/dt = k_{B_6H_{10}}[B_6H_{10}]^2$. The true second-order rate constant for the reaction, k, is related to these rate constants by the expressions $k = k_{H_2}/\nu_{H_2} = -k_{B_6H_{10}}/\nu_{B_6H_{10}}$, where ν_{H_2} and $\nu_{B_6H_{10}}$ are the stoicheiometric coefficients.[19]

fact that the data for four different reaction-vessel pressures (from 6.2 to 14.1 mmHg) are scattered about the same straight line effectively rules out any contribution to the B_{12} profile from genuine species produced in the reaction vessel, although this does *not* of course exclude the possibility of such species being formed. Further experiments showed that the B_{12}/B_6 ratio was independent of electron accelerating voltage, but decreased to zero with increase in repeller voltage, thereby confirming the assignment of the B_{12} species as a secondary-process ion formed in the mass spectrometer.

Mechanistic Considerations.—Limiting the discussion to the gas-phase reaction (as opposed to subsequent reactions involving the solid), the crucial experimental findings to be interpreted are: (*i*) the thermolysis follows second-order kinetics, *i.e.* the rate of disappearance of B_6H_{10} and the initial rate of formation of H_2 are both second order with respect to the concentration of B_6H_{10}; (*ii*) for each mol of B_6H_{10} consumed, 1 mol of dihydrogen is initially produced; (*iii*) the rate of the reaction is not suppressed by added hydrogen; (*iv*) there is a marked paucity of volatile borane products; B_5H_9 and $B_{10}H_{14}$ appear in a molar ratio of *ca.* 5:1 but more than 90% of the boron is deposited directly from the gas phase as a solid, BH_x; and (*v*) the product distribution is neither pressure- nor temperature-dependent under the conditions studied.

From these observations it seems likely that there are at least two reaction pathways involved in the thermolysis of B_6H_{10}: a major route leading to the non-volatile solid and hydrogen, and a minor route producing B_5H_9 and $B_{10}H_{14}$. Because of the relatively high thermal stability of B_5H_9 and $B_{10}H_{14}$ at the temperatures used in this work, it seems likely that they are end products of the mechanism that leads to them, and not intermediates in the formation of the solid. The major route follows second-order kinetics, and in view of the invariance of the product distribution with pressure it seems very likely that the minor route is also second order. In the absence of evidence to the contrary, there seems little justification for considering mechanisms more complex than ones involving a rate-controlling bimolecular interaction between two molecules of B_6H_{10}. The main task, therefore, is to deduce the fate of the activated complex, $(B_{12}H_{20})^\ddagger$.

Numerologically, there are many ways in which this species might disproportionate, *e.g.* (B_6 + B_6), (B_5 + B_7), (B_4 + B_8)$\cdots$(B + B_{11}), in addition to loss of dihydrogen to give $B_{12}H_{20-2n}$ + nH_2. However, only a few are chemically realistic, and these are now considered in turn, from the point of view of their possible significance in the present reaction.

(*a*) $(B_{12}H_{20})^\ddagger \rightarrow \{B_6H_8\} + B_6H_{12}$. $\{B_6H_8\}$ has not previously been suggested as a possible species, although it could conceivably act as an unstable intermediate leading to solid polymer. However, neither B_6H_{12}, nor one of its main decomposition products, B_2H_6,[9,24,25] is observed in significant amounts in the present work. Furthermore, from the very limited information available on the thermolysis of B_6H_{12}, it seems unlikely that this step could adequately account for the observed initial rate of hydrogen production.

(*b*) $(B_{12}H_{20})^\ddagger \rightarrow B_5H_9 + \{B_7H_{11}\}$. As B_5H_9 is produced in small quantity in the reaction, this route suggests itself as a possible *minor* reaction pathway. The step amounts to BH transfer from one B_6H_{10} molecule to another, and is analogous to the disproportionation proposed[26] for the ferraborane $B_5H_9Fe(CO)_3$ [equation (1)]. Transfer of BH has also been invoked for reactions involving $\{B_3H_7\}$, and a similar process has been used to explain the formation of $B_{10}H_{14}$ in the thermolysis of B_2H_6.[2]

$$2B_5H_9Fe(CO)_3 \longrightarrow B_4H_8Fe(CO)_3 + B_6H_{10}Fe(CO)_3 \quad (1)$$

The species $\{B_7H_{11}\}$ has never been observed[18] and this is consistent with calculations based on geometrical theory, which predict a structure too open to attack at exposed B atoms.[27] However, it has been suggested as a highly reactive intermediate in the formation of $B_{13}H_{19}$,[6,28] and under the present thermolysis conditions it would be likely to react rapidly with B_6H_{10} to give the same product. Alternatively, the process of BH transfer could continue as in equations (2)—(4) with

$$\{B_7H_{11}\} + B_6H_{10} \longrightarrow B_5H_9 + B_8H_{12} \quad (2)$$

$$B_8H_{12} + B_6H_{10} \longrightarrow B_5H_9 + \{B_9H_{13}\} \quad (3)$$

$$\{B_9H_{13}\} + B_6H_{10} \longrightarrow B_5H_9 + B_{10}H_{14} \quad (4)$$

successive formation of the reactive species B_8H_{12} and $\{B_9H_{13}\}$, and finally the stable borane $B_{10}H_{14}$. This mechanism is satisfyingly simple, the fate of each intermediate being to react further with B_6H_{10}, which is the only abundant borane species present and therefore the most likely molecule to be encountered in a collision. The mechanism is also in accord with experimental observation in that both B_8H_{12} and a B_9 species are detected as trace intermediates during the thermolysis. Moreover, the mechanism predicts a B_5H_9:$B_{10}H_{14}$ ratio of 4:1, *i.e.* as in equation (5), which is consistent with the approximate value recorded experimentally.

$$5B_6H_{10} \longrightarrow 4B_5H_9 + B_{10}H_{14} \quad (5)$$

Although this overall reaction scheme offers an attractive explanation for the observed distribution of the minor products, the quantitative implications must be regarded with some scepticism because the intermediates B_8H_{12} and $\{B_9H_{13}\}$ could undergo competitive condensation reactions with B_6H_{10} to yield the higher boranes $B_{14}H_{22}$ and $B_{15}H_{23}$[5b] (for which there is some mass-spectral evidence in the present work), and these in turn would be likely to polymerize further.

(*c*) $(B_{12}H_{20})^\ddagger \rightarrow \{B_4H_8\} + B_8H_{12}$. The reactive intermediate $\{B_4H_8\}$ is known[29] to add dihydrogen to give B_4H_{10}. The complete absence of the latter in the products therefore argues strongly against this step. Admittedly B_4H_{10} is known to be highly unstable under thermolysis conditions,[2] but it is unlikely that it would be so short-lived as to escape detection entirely, particularly in the lower temperature runs. In any case B_2H_6 and B_5H_{11}, which comprise the main decomposition products of B_4H_{10}, and the main volatile products of its cothermolysis with B_6H_{10} at 348 K,[9] are not observed in other than trace amounts either. Octaborane(12) *is* observed in the thermolysis, but this could be explained by the mechanism discussed in (*b*).

(*d*) $(B_{12}H_{20})^\ddagger \rightarrow \{B_3H_7\} + \{B_9H_{13}\}$. The products of this step are both non-isolable species that are seen as essential intermediates in borane interconversion reactions.[2] On the basis of their known reactions with B_6H_{10} in solution,[5b] they would be expected to react rapidly with B_6H_{10} in the thermolysis to yield B_9H_{15} and $B_{15}H_{23}$, respectively, and subsequent reactions of these two species in the presence of B_6H_{10} could well lead to the efficient production of non-volatile solids.[5b,6,18] This step therefore warrants serious consideration as a possible major route for the thermolysis of B_6H_{10}, and the early sequence of events (6)—(11) could

$$\{B_3H_7\} + B_6H_{10} \longrightarrow B_9H_{15} + H_2 \quad (6)$$

$$B_9H_{15} \longrightarrow B_8H_{12} + \{BH_3\} \quad (7)$$

$$B_8H_{12} + B_6H_{10} \longrightarrow B_{14}H_{22} \quad (8)$$

$$\{BH_3\} + B_6H_{10} \longrightarrow \{B_7H_{11}\} + H_2 \quad (9)$$

$$\{B_7H_{11}\} + B_6H_{10} \longrightarrow B_{13}H_{19} + H_2 \quad (10)$$

$$\{B_9H_{13}\} + B_6H_{10} \longrightarrow B_{15}H_{23} \qquad (11)$$

$$7B_6H_{10} \longrightarrow B_{13}H_{19} + B_{14}H_{22} + B_{15}H_{23} + 3H_2 \qquad (12)$$

be postulated to follow the rate-determining step. This corresponds to an overall reaction (12). The experimentally observed 1:1 ratio of hydrogen produced *versus* B_6H_{10} consumed could only be explained if these reactions, together with subsequent reactions of the products $B_{13}H_{19}$, $B_{14}H_{22}$, and $B_{15}H_{23}$ to produce four extra molecules of hydrogen, followed in rapid succession after the initial rate-determining bimolecular step. As already mentioned, there were indications in the mass spectra of the presence of B_{13}, B_{14}, and B_{15} species, but the peaks were extremely weak. Assuming that these species would be reasonably volatile at the temperatures concerned (393—438 K), this implies either that they exist only as transient intermediates undergoing rapid polymerization as soon as they are formed, or that the route is of negligible importance. Intuitively, the latter seems the more likely, but a definitive answer to the problem must await the results of further experiments.

(*e*) $(B_{12}H_{20})^{\ddagger} \rightarrow B_2H_6 + B_{10}H_{14}$. The virtual absence of B_2H_6 in the products of thermolysis of B_6H_{10} effectively eliminates this as a possible reaction pathway. Interestingly, B_2H_6 has been shown to react with $B_{10}H_{14}$ in the liquid phase at 373 K, *via* a postulated icosahedral $\{B_{12}H_{12}\}$ intermediate to produce non-volatile yellow solids as the only borane species.[30] However, any suggestion that step (*e*) followed rapidly by this cothermolysis might constitute the major route for the formation of the non-volatile solids in the thermolysis of B_6H_{10} is effectively ruled out by the reported stoicheiometry (13). This

$$B_2H_6 + B_{10}H_{14} \longrightarrow 4H_2 + (BH)_{12} \qquad (13)$$

would require an initial rate of hydrogen production twice that actually observed in the B_6H_{10} thermolysis. In this respect a careful study of the reaction between B_2H_6 and $B_{10}H_{14}$ in the gas phase would clearly be of interest.

(*f*) $(B_{12}H_{20})^{\ddagger} \rightarrow \{BH_3\} + \{B_{11}H_{17}\}$. In the presence of B_6H_{10} the non-isolable species $\{BH_3\}$ would probably lead to the production of $B_{13}H_{19}$ and thereafter to higher boranes as already discussed. However, the fact that B_{11} species have previously neither been isolated nor suggested as reactive intermediates in borane interconversion reactions makes this an unlikely route.

(*g*) $(B_{12}H_{20})^{\ddagger} \rightarrow nH_2 + B_{12}H_{20-2n}$ (n = 0, 1, *or* 2). The formation of a reactive B_{12} intermediate represents the simplest and most appealing initial step that can be envisaged for the major reaction leading to the solid. This would not only account for the observed order of the reaction, but would provide the most straightforward explanation for the shortage of volatile borane products. Although there is no direct mass-spectral evidence for such a species, the existence of the $B_{12}H_8^+$ ion–molecule suggests that a neutral dodecaborane is plausible.

From the initial stoicheiometry it is clear that the very early steps in the thermolysis must result on average in the elimination of one molecule of hydrogen per molecule of B_6H_{10}. This 'shake-out' process need not necessarily be complete in the initial step, and in principle the activated complex could generate any one of the reactive intermediates $\{B_{12}H_{20-2n}\}$ (where n = 0, 1, or 2). However, on the basis that the activated complex by definition represents a state of enhanced energy, it seems more likely that two molecules of hydrogen would be ejected immediately rather than in a subsequent fast, low-energy step. This would lead to $\{B_{12}H_{16}\}$, a previously unreported reactive intermediate,* *i.e.* as in equation (14). The reverse step is ruled out by the observation

$$(B_{12}H_{20})^{\ddagger} \longrightarrow 2H_2 + \{B_{12}H_{16}\} \qquad (14)$$

that the initial rate of the reaction is unaffected by the presence of added dihydrogen. The observation[31] that dideuterium does not exchange directly with B_6H_{10} at room temperature during a period of 24 h is also consistent with these conclusions, although further experiments at elevated temperatures would be desirable. Because the species $\{B_{12}H_{16}\}$ is not detected in the mass spectrum, it must (if formed) be assumed to react immediately with B_6H_{10} in a rapid series of condensation polymerization reactions satisfying the overall requirements of the initial stoicheiometry, and leading ultimately to the removal of *ca.* 90% of the boron from the gas phase.

In summary, reaction (*g*), *i.e.* the loss of dihydrogen from $(B_{12}H_{20})^{\ddagger}$, seems the most direct first step towards the production of solids from gaseous B_6H_{10}, whereas reaction (*b*) (to give initially B_5H_9 + $\{B_7H_{11}\}$) seems the most likely route to the minor gaseous products of thermolysis. Reaction (*d*) (to give initially $\{B_3H_7\}$ + $\{B_9H_{13}\}$) cannot be ruled out as a possible alternative route to the solid products, but reactions (*a*), (*c*), (*e*), and (*f*) seem unlikely to occur under the conditions used.

Conclusions

Hexaborane(10), when purified, has considerably greater thermal stability than previously reported. The thermolytic decomposition of B_6H_{10} in the gas phase at low pressures has been shown to proceed by a second-order process with an activation energy of 79.7 ± 3.7 kJ mol^{-1} and a pre-exponential factor of 4.7×10^6 m^3 mol^{-1} s^{-1}. In the initial stages the reaction produces 1 mol of hydrogen per mol of B_6H_{10} consumed, and deposits some 90% of the reacted borane from the gas phase as a non-volatile solid hydride of approximate composition $BH_{1.33}$, which then loses more hydrogen to give a solid of composition BH_x where x *ca.* 1.0. The simplest mechanism consistent with these facts involves a rate-determining bimolecular collision, with rapid elimination of two molecules of hydrogen from the $(B_{12}H_{20})^{\ddagger}$ activated complex to give $\{B_{12}H_{16}\}$, a hitherto unproposed reactive intermediate, which rapidly polymerizes in the presence of excess of B_6H_{10}. Alternative modes of deactivation of the $(B_{12}H_{20})^{\ddagger}$ complex cannot be entirely eliminated as possible routes to the production of the solid, but the evidence suggests that they are less likely. They do, however, offer plausible routes for the production of the minor amounts of B_5H_9 and $B_{10}H_{14}$ that are observed.

If it is indeed formed, the intermediate $\{B_{12}H_{16}\}$ would be the first known neutral dodecaborane.* Efforts are therefore being made to isolate this or other possible stable intermediates by means of 'hot/cold' reactions of B_6H_{10}, and by cothermolysis in the presence of 'chemical trapping agents' such as carbon monoxide. Cothermolyses with other boranes are also being carried out to resolve specific questions raised in the present study, and to gain further insight into the mechanism.

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* Since this paper was submitted, the synthesis of a neutral dodecaborane, $B_{12}H_{16}$, stable below *ca.* 65 °C, has been reported (C. T. Brewer and R. N. Grimes, *J. Am. Chem. Soc.*, 1984, **106**, 2722).

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