Interconversion of Boron Hydrides. Part 1. Thermolysis of Individual Boranes

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Low-resolution mass spectra of B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, B_8H_{12}, B_9H_{15}, and $B_{10}H_{14}$ have been recorded on a conventional spectrometer with ion-source temperatures in the range 50—60 °C. The spectra are compared with those from a molecular-beam sampling mass spectrometer. Data for ion current *versus* pressure at each unit mass have been recorded for the various boranes and argon, and a method developed for the continuous quantitative analysis of mixtures of boranes in the gas phase. The products of thermolyses of B_2H_6 at 100 and 120 °C and of B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and B_6H_{12} at 75 °C have been examined as a function of time and compared with earlier results where available.

DESPITE the thermal instability of many boron hydrides,[1,2] most mass spectrometric studies have been carried out with ion-source temperatures in the region of 250 °C or at unspecified temperatures.[3,4] Exceptions include the spectrum of $B_{10}H_{16}$ recorded on a conventional spectrometer at 100 °C,[5] and the work of Stafford and co-workers [6-10] who used a molecular-beam sampling instrument with a sample-inlet system which could operate at temperatures as low as room temperature.

As a necessary preliminary to a study of the thermolysis and cothermolysis of the boranes we have investigated the spectra of boranes by means of a conventional instrument operating with ion-source temperatures in the region 50—60 °C in order to obtain spectra as free as possible from thermolysis products. With these spectra and ion-current *versus* pressure data we have developed a technique for analysing complex mixtures of boranes quantitatively. This study reports results of work on the thermolyses of B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, and $B_{10}H_{14}$. The matter is of great importance in borane chemistry since thermolytic reactions and interconversions still provide the main routes to the higher boranes.

EXPERIMENTAL

All boranes used in this work except B_5H_9 and $B_{10}H_{14}$ were prepared by standard methods [11] and were purified and handled by means of standard vacuum-line techniques; B_5H_9 was provided by courtesy of Dr. R. E. Williams, Chemical Systems Inc., California, and $B_{10}H_{14}$ was a commercial sample (Olin Chemical Co. Ltd.) sublimed twice before use. Argon was BOC Ltd., Standard Grade.

The AEI MS30 mass spectrometer was operated under the following source conditions unless otherwise stated: 70-eV † ionising electron beam, 4-kV accelerating voltage, 300-μA trap current, temperature 50—60 °C with cooling by a constant pressure of compressed air, and ion-source pressure-gauge reading 5×10^{-8} to 1×10^{-6} mmHg.

Gaseous boranes were introduced *via* a vacuum line into a calibrated 1-l reaction vessel fitted with magnetically operated high-vacuum all-glass taps. Samples were leaked into the spectrometer through 180 mm of Veridia capillary tubing (diameter 0.1 mm) which gave a reduction in pressure by a factor of *ca.* 10^6. The reaction vessel, taps, and leak were contained in an oven which could be maintained at 30—300 °C (±0.2 °C). The glass tubing (diameter 7 mm; length *ca.* 600 mm) from the leak to the spectrometer gas-inlet probe was kept at 50 °C. For ion-current *versus* pressure data, $B_{10}H_{14}$ samples were introduced into the reaction vessel through a detachable side arm and vapourised at 75 °C. Separate experiments with the lower boranes and argon shows that ion-current *versus* reaction-vessel pressure data were the same within experimental error whether the oven was set at room temperature or 75 °C. Although the reproducibility of the abundance of each individual ion in a borane spectrum at a given pressure was in the range ±(1—5)%, the total ion-current values of repeated spectra usually agreed to within ±1%.

Low-resolution (unit-mass) spectra and ion-current *versus* reaction-vessel pressure data were measured for B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, $B_{10}H_{14}$, and argon, and are recorded in Tables 1 and 2. The spectra in Table 1 were averaged from at least seven recordings taken on different occasions. The data for ion-current *versus* pressure were collected with the multiplier set at 2.5, usually from experiments carried out on at least two separate occasions. Table 2 lists total ion current produced by 5 mmHg borane pressures in the reaction vessel relative to argon. Impure samples of B_8H_{12} and B_9H_{15} were obtained as minor products from preparations of lower boranes [11] and were in insufficient amounts for purification. Estimates of ion current *versus* pressure values were calculated from the data on the other boranes. Because of the impurities, only the parent-ion envelopes of B_8H_{12} and B_9H_{15} could be recorded satisfactorily (Table 1). These constituted *ca.* 80 and 60% respectively of the total ion currents from B_8H_{12} and B_9H_{15}. The remainder of the spectra were calculated from the published molecular-beam spectrum of B_8H_{12},[9] and the conventional spectrum of B_9H_{15}.[12] Similarly, the reported molecular-beam spectra of $\{BH_3\}$,[6] $\{B_3H_7\}$,[13] and $\{B_4H_8\}$ [10] were used (species in braces are non-isolable borane ' fragments '). Ion current *versus* pressure data were estimated for these species based on the measurements for the other boranes (Table 2). Since none of the species $\{BH_3\}$, $\{B_3H_7\}$, $\{B_4H_8\}$, B_8H_{12}, and B_9H_{15} appears in more than very small amounts during the thermolyses of the more stable boranes, these assumptions and estimates are adequate at this stage (see below).

The trend of increasing ion currents with increasing number of boron atoms (Table 2) is analogous to the reported relative-sensitivity data of hydrocarbons.[14]

Because of the possible effects of mass discrimination along the leak, all spectra of mixtures were recorded 1 min

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† Throughout this paper: 1 eV ≡ 1.60×10^{-19} J; 1 mmHg ≡ 13.6 × 9.8 Pa.

TABLE 1

Low-resolution mass spectra of boranes [a]

m/z	$B_{10}H_{14}$ [b]	B_6H_{12}	B_6H_{10}	B_5H_{11}	B_5H_9	B_4H_{10}	B_4H_{10} [c]	B_4H_{10} [d]	B_2H_6
10		1.0	1.0	1.2	1.7	1.6	1.2	9.3	6.7
11	1.2	3.7	4.6	4.0	5.5	5.8	5.9	25.8	27.0
12	1.6	1.2		1.0	1.0	1.4	0.6	9.2	13.7
13	5.8	4.5	2.8	3.3	3.5	5.2	3.6	19.7	34.2
22		0.2					0.9	2.3	15.3
23		2.5		1.8	1.0	2.5	2.4	5.7	101.3
24		4.7		3.2	1.5	5.0	5.0	9.0	207.2
25		3.3		2.7	1.1	3.9	4.0	4.4	84.6
26		5.1	0.8	4.9	1.0	4.1	4.0	4.3	176.8
27		9.9	1.6	8.5	1.8	7.6	5.9	7.1	333.2
28									trace
32		1.4				1.3	1.5	2.5	
33		1.4		1.4	1.2	3.4	3.7	12.8	
34		4.7	1.6	4.1	3.8	12.1	12.5	29.5	
35		8.2	2.5	7.3	5.3	19.6	23.1	45.3	
36		9.3	2.5	7.8	4.5	21.4	23.2	40.5	
37		9.1	1.7	14.3	2.3	31.8	30.0	38.2	
38		9.9	1.6	16.8	1.0	39.2	32.6	35.1	
39		7.6		2.5		5.8	3.6	2.8	
40									
41		0.6							
42		1.0		1.2	1.3	3.0	2.7	4.5	
43		3.5	1.6	3.5	3.5	8.5	8.6	14.9	
44		6.8	3.1	7.3	7.3	17.2	19.6	31.2	
45		13.0	5.7	13.6	13.2	28.1	32.1	46.9	
46	1.0	21.2	7.9	23.3	19.3	46.8	56.4	56.6	
47		31.7	12.6	39.0	35.6	96.5	95.0	110.0	
48		29.0	11.0	38.0	31.9	100.6	136.5	127.3	
49		24.5	8.6	24.4	7.8	231.4	208.3	124.2	
50		22.2	7.9	18.9	3.2	230.7	212.7	126.8	
51		6.2	1.6	4.7		43.5	44.5	41.1	
52		4.5	0.8	3.0	2.3	19.3	18.4	11.7	
53		5.8	3.8	6.5	9.4	1.7	1.5	1.2	
54		13.0	8.8	14.6	20.9	trace	trace		
55	1.9	16.7	11.8	20.6	26.4				
56	3.9	22.6	15.6	23.3	29.7				
57	3.3	25.3	18.6	28.6	31.7				
58	3.8	33.4	27.2	55.6	71.7				
59	2.5	43.4	40.6	95.6	123.7				
60		33.4	30.5	104.9	99.5				
61		31.3	24.8	129.5	114.2				
62		26.1	21.7	118.9	97.0				
63		12.8	26.1	78.6	120.3				
64		10.1	20.1	61.0	93.9				
65	1.1	12.4	13.4	1.2					
66	1.7	19.6	23.3	trace					
67	2.1	21.0	25.3						
68	2.5	21.6	31.9						
69	1.9	26.6	42.9						
70	1.2	50.9	74.8						
71		76.9	110.8						
72		64.5	87.7						
73		58.9	79.4						
74		45.7	67.6						
75	1.6	36.9	67.1						
76	2.4	28.4	45.0						
77	3.3	8.7							
78	4.1 [b]	2.1							

[a] Ions recorded under conditions (50 °C, *etc.*) described in the Experimental section unless stated otherwise; trace amounts refer to <0.1% of total ion current. The following data were also collected [*m/z* (intensity)]: B_9H_{15}, 99 (21), 100 (22), 101 (26), 102 (35), 103 (59), 104 (91), 105 (94), 106 (69), 107 (90), 108 (118), 109 (78), 110 (78), 111 (47), 112 (50), 113 (47), 114 (35); B_8H_{12}, 88 (27), 89 (37), 90 (53), 91 (80), 92 (107), 93 (103), 94 (84), 95 (100), 96 (117), 97 (117), 98 (87), 99 (60), 100 (27). [b] The spectrum of $B_{10}H_{14}$ continues [*m/z* (intensity)]: 79 (3.7), 80 (2.6), 81 (1.5), 82 to 84 (—), 85 (2.0), 86 (4.2), 87 (6.7), 88 (7.7), 89 (9.1), 90 (8.9), 91 (7.2), 92 (3.7), 93 (1.5), 94 (—), 95 (1.8), 96 (4.5), 97 (8.9), 98 (13.3), 99 (17.8), 100 (21.6), 101 (21.0), 102 (16.6), 103 (11.4), 104 (8.6), 105 (6.0), 106 (4.6), 107 (7.0), 108 (12.3), 109 (16.0), 110 (16.7), 111 (18.1), 112 (23.9), 113 (35.6), 114 (49.5), 115 (60.1), 116 (69.3), 117 (67.4), 118 (61.0), 119 (74.0), 120 (89.1), 121 (79.2), 122 (47.0), 123 (22.7), 124 (9.3). [c] Molecular-beam spectrum.[8] [d] Conventional spectrum.[8]

after opening the tap between the reaction vessel and leak. Separate investigations using mixtures of ($Ar + CH_4 + CCl_4$), ($Ar + B_2H_6 + B_5H_9$), and ($Ar + B_4H_{10} +$ other boranes) showed that satisfactory sampling was occurring without significant fractionation at this time (see Table 3). Argon was used as an internal calibrant since it was unreactive, and had a simple spectrum which did not interfere with those of the boranes. Calculation of partial pressures of borane species was always carried out by referring to the standard ion current *versus* pressure data recorded at a multiplier setting of 2.5. After several such calculations had proved satisfactory, a computer program was written

TABLE 2

Total ion current (relative to that of argon $\equiv$ 100 at 5 mmHg) from 5 mmHg borane pressure in the reaction vessel

Borane	$B_{10}H_{14}$ *	B_6H_{12}	B_6H_{10}	B_5H_{11}
Relative total ion current	402	538	546	580
Borane	B_5H_9	B_4H_{10}	B_2H_6	
Relative total ion current	559	512	199	

* This value is for 0.25 mmHg of $B_{10}H_{14}$ since pressures greater than 0.3 mmHg were not studied for this borane.

TABLE 3

Comparison of mass-spectrometrically determined partial pressures of mixtures of boranes and argon with values calculated by direct manometric metering

	Pressure (mmHg)	
	Measured manometrically	Found mass spectrometrically
Mixture 1		
Argon	2.49	2.50
B_2H_6	3.17	3.32
B_4H_{10}	3.26	3.37
Mixture 2		
Argon	2.30	2.30
B_4H_{10}	2.59	2.64
B_5H_{11}	2.57	2.39

enabling the partial pressures of individual boranes in a mixture to be calculated from low-resolution data.

The m values of the observed relative ion current (B_i) in any given mass spectrum are derived from a summation of the corresponding values of the n component spectra (A_{ij}) normalised by appropriate factors (X_j). Provided that $m \gg n$, the simultaneous linear equations $AX = B$ can be solved by a suitable algorithm to obtain a least-squares solution for the values X_j, and thence to derive the fraction of the total ion current due to each of the n components in the mass spectrum. Although this procedure can be applied to the whole of the spectrum, it is preferable in some circumstances to adopt a 'spectrum-stripping' approach. Thus the contribution from $B_{10}H_{14}$ can be determined in isolation by considering only masses 115—124 (which in any case are the major contribution). The value of X_j obtained is then used to subtract out the $B_{10}H_{14}$ contribution at lower masses. The process is repeated for B_9H_{15} between 101 and 114, *etc.* Alternatively, masses 101—124 can be used to obtain $B_{10}H_{14}$ and B_9H_{15} simultaneously, *etc.* However, it is always necessary to couple together such pairs as B_6H_{12} and B_6H_{10}, B_5H_{11} and B_5H_9, or B_4H_{10} and $\{B_4H_8\}$ because of the almost total overlap of their spectra. The program was written to treat this in a general form, the whole operation being specified by the appropriate cut-off masses which in the present instance were selected from the values 10, 14, 28, 40, 54, 66, 78, 100, 114, and 124. The component spectra were selected upon demand from a master data file.

The calibration data for argon and the major boranes of partial pressure *versus* ion current were converted into the coefficients of Chebyshev polynomials of degree k (k being chosen to give the best representation of the data for each borane) and incorporated into the program to allow interconversion in either direction. Using the polynomial for argon, the calculated value for the total relative ion current (ΣB) in each spectrum was normalised so that the ion current for mass 40 (argon) corresponded to the partial pressure of argon in the mixture. All the ion currents were then further normalised so that the ion current at time $t = 0$ corresponded exactly to the partial pressure of the borane in the reaction vessel. The normalised fractional ion currents were then converted directly into partial pressures using the calibration data. Partial pressures for B_9H_{15} and B_8H_{12} were calculated from the $B_{10}H_{14}$ calibration data using estimated scaling factors of 1.11 and 1.25 respectively, $\{B_4H_8\}$ and $\{B_3H_7\}$ from B_4H_{10} data using 1.01 and 1.35 respectively, and $\{BH_3\}$ from B_2H_6 data using 1.3. The errors introduced thereby are small compared to the experimental error for these minor components.

The numerical methods used do not provide standard-deviation data but, in general, self-consistent results were obtained to within an accuracy of *ca.* 0.5% of the total pressure of the boranes.

Sometimes problems were encountered in mixtures containing both the pentaboranes or both the hexaboranes because of the similarity of their spectra. These problems could be overcome by measuring the relative amounts of each component in a separate experiment under high resolution. For the pentaboranes the ions at a mass-to-charge ratio of 64—66 were used. Taking m/z 64 as an example, we find only $[^{11}B_5{}^1H_9]^{+\cdot}$ present from B_5H_9, whereas from B_5H_{11} appreciable amounts of $[^{11}B_5{}^1H_9]^{+\cdot}$, $[^{11}B_4{}^{10}B^1H_{10}]^{+\cdot}$, and $[^{11}B_3{}^{10}B_2{}^1H_{11}]^{+\cdot}$ are observed. Using the ratios of the intensities of these various ions separated under high resolution we could determine the presence or absence of B_5H_{11} and calculate the ratio of B_5H_9 to B_5H_{11} when both were present. Similarly, for the hexaboranes, ions at m/z 76—78 were examined.

During this work we were unable to positively identify the presence of any of the intermediates $\{BH_3\}$, $\{B_3H_7\}$, or $\{B_4H_8\}$ in significant amounts (*i.e.* >0.5% of the total pressure of boranes).

Hydrogen was a product from all thermolytic decompositions but was not analysed quantitatively. A thin layer of a pale yellow, solid, involatile substance, as yet unidentified, was deposited during the course of the reactions. It had no apparent effects on subsequent reactions. Such deposits are well known from thermolysis of boranes [15-17] and were not analysed in this study.

The mass spectra of thermolysis reaction products were scanned from below mass 10 to above mass 124 for all points after initial time zero. Products at higher mass (*i.e.* >$B_{10}H_{14}$) were looked for periodically but not found. Numerous previous other studies have shown these reactions to be homogeneous.[1,2]

RESULTS AND DISCUSSION

Mass Spectra.—The spectra of B_4H_{10}, B_5H_9, B_5H_{11}, and B_6H_{12} are remarkably similar to the published molecular-beam spectra.[7,8,10] Parent molecular ions were observed and there was less fragmentation than previously reported with conventional instruments.[3,4] The differences noted earlier [7,8] between the spectra of B_4H_{10} obtained on a molecular-beam instrument and a conventional spectrometer were mainly attributed to thermolysis in the inlet system and ion source of the latter. The present work shows that a spectrum of B_4H_{10} which is almost identical to the molecular-beam spectrum can be obtained on a conventional machine by limiting the ion-source temperature to 50—60 °C (see

Table 1). Some differences are to be expected in spectra obtained on different machines and the small discrepancies found between the spectra of the pentaboranes may be of the expected magnitude.[10] However, B_2H_6, B_5H_9, and B_5H_{11} all gave relatively higher abundances of parent molecular ions and less fragmentation when lower temperatures were used in the ion source. In the case of B_6H_{12} the spectrum in Table 1 is intermediate between the molecular beam and 'conventional' spectra reported by Steck *et al.*[9] It contains a more significant proportion of ions in the region m/z 52—64 than does the molecular-beam spectrum. The structure of B_6H_{12} postulated from n.m.r. spectra is similar to B_5H_{11} with one bridging hydrogen replaced by a BH_2 group.[18] Thus the loss of BH_n species may be expected to occur relatively easily from $[B_6H_{12}]^{+\cdot}$ and significant contributions from B_5-containing ions could result. It has been noted that loss of BH_n species is more important from B_5H_{11} than from B_5H_9, and in general B_nH_{n+6} boranes produce more abundant fragment ions containing less than n B atoms than do corresponding B_nH_{n+4} boranes.

It is clear from our results that the spectra of the boranes recorded at low source temperatures are reproducible and do not contain significant amounts of thermolysis products. Previously published spectra of B_nH_{n+6} boranes at *ca.* 250 °C almost certainly contain contributions from thermolysis products.

Thermolysis of B_2H_6.—Reactions were carried out at 100 and 120 °C with a B_2H_6 pressure of 11 mmHg. Major products were B_5H_9, B_5H_{11}, and $B_{10}H_{14}$. Smaller amounts of B_4H_{10} were observed from both reactions and trace amounts (0—0.4%) of hexaboranes, B_8H_{12}, and B_9H_{15} were found from the reaction at 100 °C. The change in concentration with time (5 000 min) of the more important constituents in the reaction at 120 °C is shown in a Figure deposited in Supplementary Publication No. SUP 22541 (4 pp.).* The reaction at 100 °C was similar but much slower. The general shapes of the curves for B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11} agree with comparable previous work carried out at 111[15] and 110 °C.[16] However, neither the study using g.l.c. analysis[15] nor that using a mass spectrometric method[16] analysed for any boranes other than B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11}. Further, the earlier mass spectrometric method could not distinguish between B_5H_{11} and a mixture of B_5H_{11} with a small amount of B_4H_{10} and so could not identify B_4H_{10} with certainty. Our more sophisticated approach has enabled us to identify small amounts of products (hexaboranes, B_8H_{12}, and B_9H_{15}) known to be produced in the thermolysis of B_2H_6.[17,19] In addition to the products we observed, heptaboranes and possibly a trace of $B_{20}H_{26}$ were reported from the shock-tube thermolysis of B_2H_6.[20] We found no evidence for heptaboranes or $B_{20}H_{26}$ and feel confident that we would have observed $B_{20}H_{26}$ had it been present, even in trace amounts, in our reactions.[21]

It is not our intention at this stage to draw conclusions regarding the mechanism of interconversion of the boranes since this requires a more detailed consideration of the thermodynamics and kinetics of these complex systems. Rather the present study is aimed at developing a technique for the acquisition of such detailed information. The problems faced in assessing possible mechanisms before such information is available are amply illustrated by the appearance of B_4H_{10} in the thermolysis of B_2H_6. As Schaeffer has pointed out,[22] the relatively small amount of B_4H_{10} observed during thermolysis at 100—120 °C is probably a function of its high reactivity rather than its formation by decomposition of a higher borane precursor, *i.e.* B_5H_{11}, as might be supposed from an initial examination of the data. Our work suggests that the reactivity of B_4H_{10} would make a study at 100 °C difficult and we therefore proceeded to investigate its thermolysis at 75 °C. At this temperature the thermolysis of B_2H_6 was very slow indeed.

Thermolysis of B_4H_{10} *at* 75 °C.—Tetraborane(10) decomposes rapidly at 75 °C. An initial pressure of 3 mmHg of B_4H_{10} was used. The variation with time (425 min) of the major constituents B_2H_6, B_4H_{10}, pentaboranes (mainly B_5H_{11}), hexaboranes, and $B_{10}H_{14}$ is shown in a Figure deposited in SUP 22541. The concentration of B_5H_{11} rose rapidly to a maximum of 1.0 mmHg after *ca.* 60 min and then slowly decreased to 0.8 mmHg after 425 min. Likewise the concentration of hexaboranes rose to a maximum of 0.3 mmHg after 50 min and then slowly decreased to 0.1 mmHg after 425 min. In contrast, the amount of B_2H_6 increased progressively throughout the reaction period, being 0.2 mmHg after 50 min and 0.65 mmHg after 425 min. Decaborane(14) was formed at a similar rate during the first 120 min (0.3 mmHg) but then, perhaps surprisingly, diminished slightly to 0.2 mmHg. Trace amounts of B_8H_{12}, B_9H_{15}, and a yellow polymeric material were also observed during the reaction but no heptaboranes were detected. Similar results were obtained from a reaction with an initial pressure of B_4H_{10} of 11 mmHg. A previous study of B_4H_{10} thermolysis using a molecular-beam spectrometer fitted with a flow reactor found B_2H_6, $\{B_4H_8\}$, pentaboranes, hexaboranes, heptaboranes, B_8H_{12}, and $B_{10}H_{14}$ present with possibly a B_9-containing compound, although these compounds could not be quantitatively analysed with the method used.[7] Other workers studying the kinetics of decomposition of B_4H_{10}[23-25] at temperatures comparable to the present study have reported and in some cases analysed for B_2H_6, B_5H_9, B_5H_{11}, hexaboranes (probably B_6H_{12}),[24] $B_{10}H_{14}$, and a yellow polymeric material in the products. Comparison with these studies further implies that under the conditions used in the present work the initial rate of decomposition of B_4H_{10} is first order and would be expected to be independent of the concentration of B_2H_6 and B_5H_{11}. However, none

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

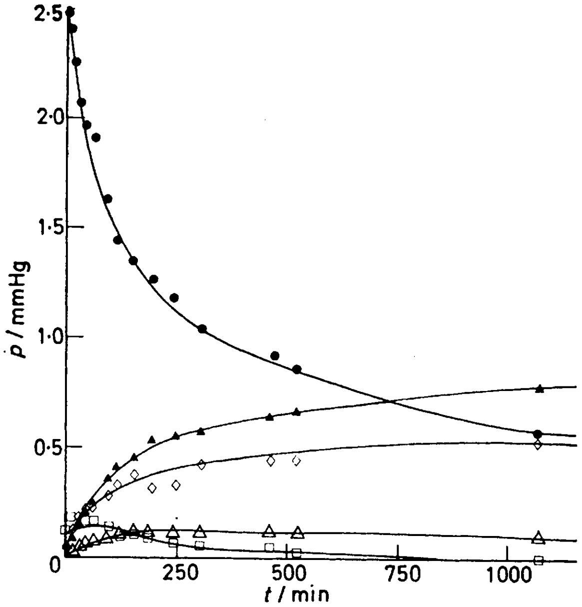

FIGURE 1 Thermolysis of B_5H_{11} at 75 °C. Boranes: B_5H_{11} (●), B_2H_6 (▲), B_5H_9 (◇), $B_{10}H_{14}$ (△), and B_6H_{10}–B_6H_{12} (□)

of this previous work includes quantitative analysis for hexaborane species, although the present results show that, for the first 50—60 min, these are the second most abundant products. We intend to investigate this reaction in more detail.

Thermolysis of B_5H_9 *at* 75 °C.—No thermolysis products were observed from 10 mmHg of B_5H_9 held at 75 °C for 12 h. This is consistent with previous results.[10,26] At higher temperatures (200—228 °C) and pressures (40—80 mmHg), B_5H_9 is known to produce an involatile solid of composition $(BH_{0\cdot6})_x$ and hydrogen.[26]

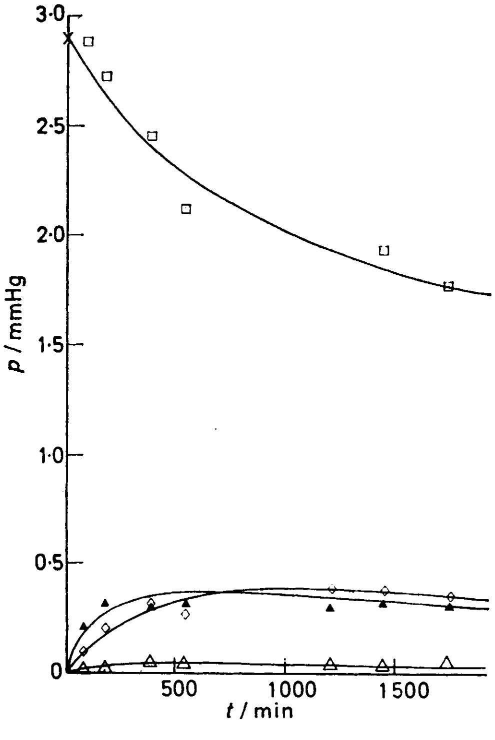

FIGURE 2 Thermolysis of B_6H_{10} (×) at 75 °C. Other boranes as in Figure 1

Thermolysis of B_5H_{11} *at* 75 °C.—The major products of thermolysing B_5H_{11} were B_2H_6, B_5H_9, and $B_{10}H_{14}$ (Figure 1). Hexaboranes were minor products and a trace of B_8H_{12} was observed. The absence of B_4H_{10} is notable.

A molecular-beam study of B_5H_{11} thermolysis at 20—500 °C in a flow reactor had previously shown $\{B_4H_8\}$ and $\{BH_3\}$ to be present, and B_2H_6 and B_5H_9 as the only stable borane products.[10] It is difficult to understand why $B_{10}H_{14}$ was unobserved in the previous study since it was formed continuously in the present work and at a much faster rate than would be expected if it was produced from the B_6H_{12} (~5%) impurity in the B_5H_{11} used (see below).

Thermolysis of B_6H_{10} *at* 75 °C.—Decomposition of B_6H_{10} produced B_2H_6 and pentaboranes (mainly B_5H_9) as major products with a small amount of $B_{10}H_{14}$ and slight traces of B_8H_{12} (Figure 2). The reaction was relatively slow. The absence of B_9H_{15} and the small amount of $B_{10}H_{14}$ are suggestive of the lack of appreciable amounts of $\{B_3H_7\}$ or $\{B_4H_8\}$ occurring in the system since B_9H_{15} is the major product from reaction of B_6H_{10} and $\{B_3H_7\}$ or $\{B_4H_8\}$ at room temperature,[27] and conversion of B_9H_{15} into $B_{10}H_{14}$ by B_2H_6 has been reported.[28] Kinetic studies at present being undertaken should clarify this situation.

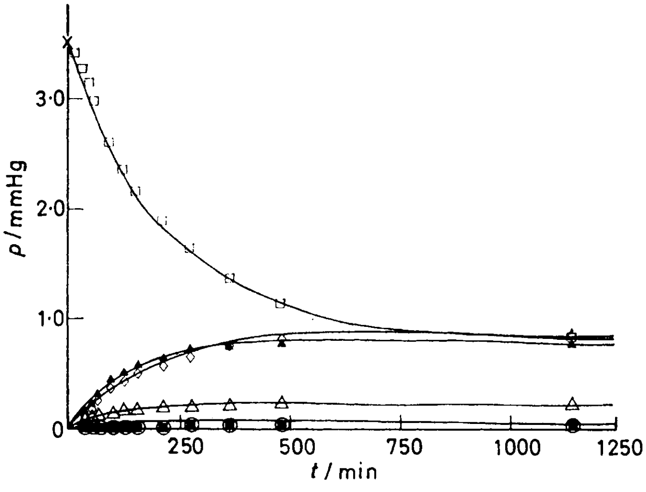

FIGURE 3 Thermolysis of B_6H_{12} (×) at 75 °C. Other boranes as in Figure 1 plus B_8H_{12} (■) and B_9H_{15} (○)

Thermolysis of B_6H_{12} *at* 75 °C.—Figure 3 shows the variation of product concentrations with time for the thermolysis of B_6H_{12} at 75 °C. Major components were B_2H_6, B_5H_9, and $B_{10}H_{14}$. Additionally, trace amounts of B_8H_{12} and B_9H_{15} were observed. Decomposition of B_6H_{12} in the gas phase has previously been reported to give small amounts of B_2H_6, B_4H_{10}, B_5H_{11}, and higher, unspecified, boranes after 1 h at 25 °C,[29] or B_5H_9 from dynamic thermolysis at 145 °C.[30] In the condensed phase at 25 °C small amounts of B_2H_6, B_4H_{10}, B_5H_{11}, and higher unidentified boranes were found.[29] At 100 °C only B_5H_9 and $B_{10}H_{14}$ were observed with no evidence of B_5H_{11}.[30]

Thermolysis of B_8H_{12}, B_9H_{15}, *and* $B_{10}H_{14}$.—The present work did not include a study of B_8H_{12} or B_9H_{15}. Previous investigations using mass spectrometric sampling from a reaction vessel at 30 °C showed B_9H_{15} to decompose primarily to B_8H_{12} which gave several uncharacterised products one of which may have been B_6H_{10}.[12]

At 75 or 100 °C no decomposition products were observed from $B_{10}H_{14}$. Higher temperatures (170—238 °C) have been reported to produce polymeric boranes which could not be satisfactorily characterised.[31] Later work has shown that $B_{20}H_{26}$ isomers are produced in 10—15% yield from thermolysis at 180—185 °C for 5 d.[32]

To summarise, we have developed a technique for analysing mixtures of boranes such as those encountered in thermolysis reactions. This will enable detailed kinetic studies to be undertaken of the thermolysis and cothermolysis of boranes, and should lead to a better mechanistic understanding of the complex series of reactions involved. The initial results presented here, together with the previous observations, suggest that thermolytic stability decreases in the sequence $B_{10}H_{14}$, $B_5H_9 \gg B_2H_6 > B_6H_{10} \gg B_6H_{12} > B_5H_{11} \gg B_4H_{10} \ggg \{B_4H_8\}$, $\{B_3H_7\}$, $\{BH_3\}$. The positions of B_8H_{12} and B_9H_{15} in this series are somewhat uncertain at present.

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