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Kinetic studies of reactions of hexaborane(10) with other binary boranes in the gas phase

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Dedicated to Professor Sheldon G. Shore on the occasion of his 70th birthday in appreciation of his outstanding contributions to the chemistry of the boron hydrides.

Abstract

Cothermolysis reactions of B_6H_{10} with the binary boranes B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11} have been studied by a quantitative mass-spectrometric technique to gain insight into the role of B_6H_{10} in borane interconversion reactions. Except in the B_6H_{10}–B_5H_9 system the initial rate of consumption of B_6H_{10} was found to be considerably more rapid than in the thermolysis of B_6H_{10} alone, indicating that interactions were occurring. Detailed kinetic studies of the B_6H_{10}–B_2H_6 and B_6H_{10}–B_4H_{10} reactions showed that the rate of consumption of B_6H_{10} was governed in each case by the rate-determining step in the decomposition of the co-reactant, the orders being 3/2 with respect to B_2H_6 and 1 with respect to B_4H_{10}; a considerable increase in the conversion of B_6H_{10} to $B_{10}H_{14}$ at the expense of polymeric solids was also observed. Added hydrogen was found to have very little effect on the reaction rates and product distributions in the cothermolysis reactions, in marked contrast to its effect on the reactions of B_2H_6 and B_4H_{10} alone. The kinetic results are entirely consistent with earlier suggestions, based on qualitative observations, that the reactive intermediates $\{B_3H_7\}$ and $\{B_4H_8\}$ are scavenged by reaction with B_6H_{10}, and suggest strongly that this borane, unlike B_6H_{12}, plays a pivotal role in the build-up to $B_{10}H_{14}$ and other higher boranes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hexaborane(10); Binary boranes; Thermolysis; Kinetic studies; Mechanism

1. Introduction

The virtual absence of one or more species intermediate between the pentaboranes and $B_{10}H_{14}$ in the thermal decomposition of B_2H_6 is an intriguing feature of this complex reaction, and raises the question of the role of the hexaboranes, B_6H_{10} and B_6H_{12}, in borane interconversions. Previous work in this laboratory has shown that these two boranes differ markedly from one another in their thermal stabilities and in the details of their individual gas-phase decompositions. Hexaborane(10), when pure, is comparable in stability to B_2H_6 itself, decomposing only slowly at 373 K in a second-order process which results in the deposition of some 90% of the boron as a non-volatile solid hydride [1–3]. Hexaborane(12), on the other hand, decomposes rapidly at this temperature in a first-order reaction which generates, almost exclusively, the volatile products B_5H_9 and B_2H_6 [4]. Whereas B_6H_{12} itself appears not to be involved in the stepwise build-up to $B_{10}H_{14}$ [5] it has been suggested [6] that B_6H_{10} may play a crucial role in the overall thermolysis of B_2H_6, by virtue of its known tendency (albeit under somewhat different conditions) to react as a Lewis base [7,8] with acidic borane intermediates such as $\{BH_3\}$, $\{B_3H_7\}$, $\{B_4H_8\}$, B_8H_{12} and $\{B_9H_{13}\}$ to produce larger boranes such as $B_{13}H_{19}$, $B_{14}H_{22}$ and $B_{15}H_{23}$. However, there have been no gas-phase studies, even of a qualitative nature, to test these ideas in any systematic way. We have therefore carried out a comprehensive investigation of cothermolysis reactions of B_6H_{10} with the small binary boranes B_2H_6, B_4H_{10}, B_5H_9 and B_5H_{11} to address this problem. The

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B_6H_{10}–B_2H_6 and B_6H_{10}–B_4H_{10} systems were studied in quantitative detail at various temperatures to obtain kinetic parameters, and the effect of adding an excess of hydrogen to each system was also investigated. Data were also recorded for the thermolysis of pure B_2H_6, which has been studied many times in the past [9] to provide a self-consistent set of initial-rate data and rate constants for direct comparison with the results obtained in the B_6H_{10}–B_2H_6 cothermolysis study. The results on these various systems, some of which have been discussed elsewhere in a preliminary form [1] provide new insights into the role of B_6H_{10} in borane interconversions.

2. Experimental

The quantitative mass-spectrometric techniques used in this work have been described in detail elsewhere [2,5,10]. Thermolyses were carried out in a pre-conditioned spherical Pyrex bulb (volume ca. 1 dm^3) in the presence of a large background of an inert-gas mixture (partial pressure 100 mmHg) comprising helium, argon and krypton in the relative proportions 98.0:1.0:1.0. [11] [For conversion to SI, 1 mmHg $\approx$ 133.322 Pa.] The gases were pre-mixed in a similar bulb at room temperature and expanded into the preheated reaction vessel, from where the mixture was continuously sampled. To facilitate adequate mixing, and to minimise premature interaction of the reactants in the liquid phase, the heavier component (B_6H_{10}) was always frozen onto the upper surfaces of the mixing bulb and the lighter component onto the lower surfaces. The inert-gas or inert-gas–hydrogen mixture was introduced into the vessel containing the frozen boranes at 77 K, before the mixture was allowed to warm to room temperature.

The boranes were prepared by methods described in the literature (B_2H_6 [12], B_4H_{10} [13], B_6H_{10} [14]) and manipulated by standard grease-free vacuum-line techniques. Purification was achieved by trap-to-trap fractionation, followed where necessary by fractionation on a low-temperature column.

3. Results and discussion

3.1. Thermolysis of B_2H_6

In agreement with earlier studies [9] the major products of the thermolysis of B_2H_6 at temperatures in the range 398–453 K were found to be H_2, B_5H_9, B_5H_{11}, $B_{10}H_{14}$ and traces of B_6H_{10}, B_6H_{12}, B_8H_{12} and B_9H_{15}. Mass-balance calculations indicated that 40–50% of the boron was deposited as involatile solid hydride. Initial-rate data, obtained by the tangent method from plots of the type shown later for the cothermolysis reactions (Figs. 2–4), are recorded in Table 1 for the thermolysis of B_2H_6 alone and in the presence of added H_2. From log–log plots of the initial rates of consumption of B_2H_6 and production of H_2 against the initial concentration of B_2H_6, the order of the reaction at 398 and 422 K was shown to be consistent with the consensus value [9] of 3/2. This value has therefore been used in

Table 1
Initial-rate data and $^3/_2$-order rate constants for thermolysis of B_2H_6 alone and in the presence of added H_2

T/K ($\pm$0.5)	$p_o(B_2H_6)$ (mmHg [a])	$-(d[B_2H_6]/dt)_o$ [b]	$(d[H_2]/dt)_o$ [b]	$10^4k_{3/2,B_2H_6}$ [c]	$10^4k_{3/2,H_2}$ [c]
		$\mu mol\ m^{-3}\ s^{-1}$		$mol^{-1/2}\ m^{3/2}\ s^{-1}$	
398.4	1.72	3.0	1.2	1.66	0.68
397.1	3.45	6.3	[d]	1.21	[d]
398.5	6.90	15.8	7.5	1.08	0.51
398.4	13.95		21.8	[d]	0.52
407.1	3.50	9.3	4.1	1.81	0.80
421.9	1.76	14.1	4.5	8.24	2.65
421.8	3.53	42.1	12.7	8.57	2.58
422.1	7.00	91.0	34.1	6.63	2.49
421.9	14.00	214.7	107.1	5.54	2.76
v423.6	3.52	27.9	[d]	5.75	[d]
423.6 [e]	3.49	8.1	[d]	1.69	[d]
437.7	3.49	76.8	51.9	16.72	6.80
451.1	3.46	125.0	112.9	28.88	26.17

[a] Initial-rates accurate to within ca. 10%.

[b] Errors in initial pressures ca. $\pm$1%. To convert pressure in mmHg to concentration in mol m^{-3} multiply by 16.03/(T/K).

[c] Evaluated from the expressions $k_{3/2,B_2H_6} = -(d[B_2H_6]/dt)_o/[B_2H_6]_o^{3/2}$ and $k_{3/2,H_2} = (d[H_2]/dt)_o/[B_2H_6]_o^{3/2}$.

[d] Data not recorded.

[e] Thermolysis carried out in presence of added H_2, $p_o(H_2) = 50.0$ mmHg.

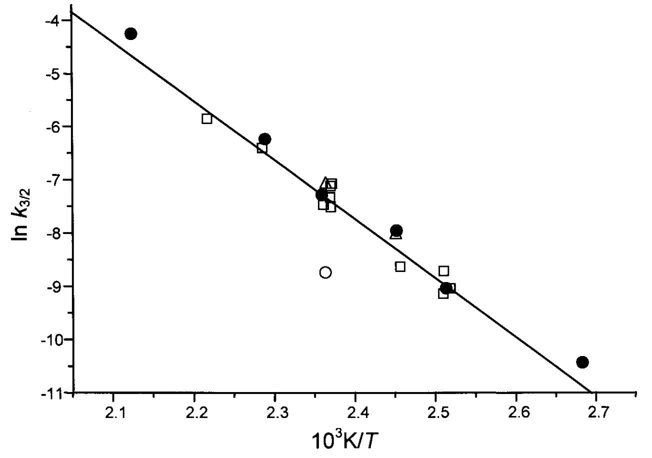

Fig. 1. Arrhenius plots for the thermolysis of pure B_2H_6 (□) and B_2H_6 in the presence of B_6H_{10} (●). For comparison, data points are also shown for a single thermolysis of B_2H_6 (p_0 3.49 mmHg) in the presence of a background of H_2 (p_0 50 mmHg) (○), and for the B_6H_{10}–B_2H_6 cothermolysis in the presence of a background of H_2 (△); details are given in Table 3. The solid line is a least-squares fit to the data obtained from the thermolysis of pure B_2H_6 (□).

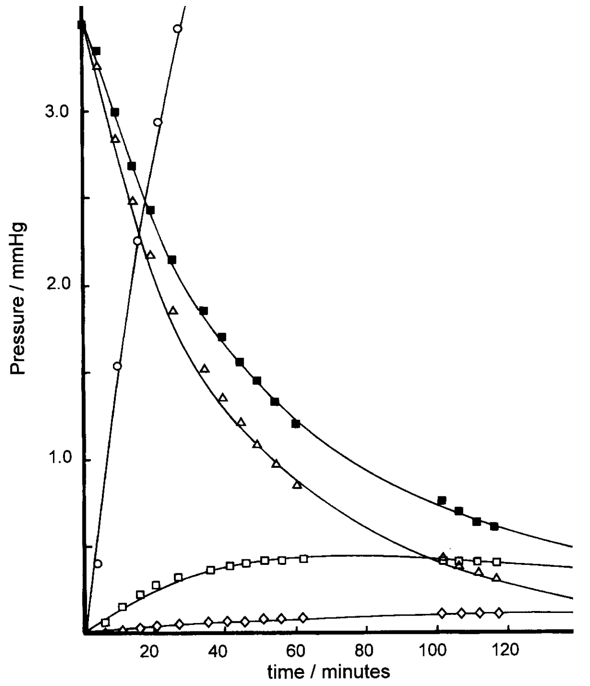

Fig. 2. Product analysis as a function of time for the cothermolysis at $T = 424.9$ K of B_6H_{10} (p_0 3.51 mmHg) with B_2H_6 (p_0 3.49 mmHg): (■) B_2H_6, (△) B_6H_{10}, (○) H_2, (◇) B_5H_9, (□) $B_{10}H_{14}$.

the calculation of all the rate constants listed in Table 1, though it is realised that this may not apply strictly to the experiments involving added H_2.

The 3/2-order rate constants for the thermolysis of B_2H_6 are shown in the form of an Arrhenius plot in Fig. 1. Least-squares analysis of these data yields a value of 92 ± 6 kJ mol^{-1} for the activation energy, and a value of $e^{18.8 \pm 1.7}$ (ca. 1.49×10^8) $m^{3/2}$ $mol^{-1/2}$ s^{-1} for the pre-exponential factor. The corresponding values from the H_2-production data are 112 ± 7 kJ mol^{-1} and $e^{23.9 \pm 2.0}$ (ca. 2.4×10^{10}) $m^{3/2}$ $mol^{-1/2}$ s^{-1}. The latter are regarded as being of limited value because the hydrogen data measure not only the homogeneous gas-phase reaction but also a contribution from the decomposition of solid hydride deposited on the surface of the reaction vessel during the reaction; the data are also complicated by the fact that the initial composition of the solid hydride is temperature dependent.

In agreement with earlier work, the thermolysis of diborane was found to be inhibited by the addition of hydrogen. This is apparent from Table 1 and Fig. 1 for the pair of experiments carried out at 423.6 K. Addition of H_2 at a partial pressure of 50 mmHg is seen to retard the rate of decomposition of B_2H_6 (p_0 3.5 mmHg) by a factor of 3.4; this run is represented by the open circle in Fig. 1.

3.2. Cothermolysis of B_6H_{10} with B_2H_6

A typical concentration-time profile for the B_6H_{10}–B_2H_6 reaction is shown in Fig. 2. In this example the co-reactants were at the same partial pressure of ca. 3.5 mmHg. Profiles for the numerous other runs in this and the other systems referred to later, in which the partial pressures are varied, are available elsewhere [15].

The main boron-containing product in this reaction is $B_{10}H_{14}$, which in some cases accounts for up to ca. 60% of the boron consumed. This compares with a value of less than ca. 5% in the thermolyses of either reactant alone [2,10]. The most efficient conversion to $B_{10}H_{14}$ occurs in those runs in which the initial concentration of B_2H_6 is greater than that of B_6H_{10}. Hydrogen is produced in quantity, and B_5H_9 ($< 5\%$) is also observed, together with trace amounts of B_8H_{12}, *n*-B_9H_{15} and the higher boranes $B_{15}H_{23}$ and $B_{16}H_{20}$. Non-volatile solid is produced in all reactions, the amounts depending on the temperature and the initial concentrations of the reactants. Mass-balance calculations indicate a composition of approximately $BH_{1.5}$.

Inspection of the initial-rate data in Table 2 reveals that the rate of consumption of B_2H_6 at any given temperature and initial pressure is, within experimental error, the same as that observed in the thermolysis of B_2H_6 alone (see Table 1), and essentially independent of the concentration of B_6H_{10}. By contrast, the rate of consumption of B_6H_{10} is invariably faster than in the thermolysis of B_6H_{10} alone, and depends dramatically on the concentration of B_2H_6.

In an attempt to gain a better understanding of the nature of the interaction between B_6H_{10} and B_2H_6, reaction orders have been determined from plots of the log of the initial rate of consumption of B_2H_6 against the log of the initial concentrations of each reactant.

Table 2
Initial-rate data for cothermolysis of B_2H_6 and B_6H_{10} with and without added H_2 [a]

T/K	$p_o(B_2H_6)$	$p_o(B_6H_{10})$	$p_o(H_2)$	$-(d[B_2H_6]/dt)_o$	$-(d[B_6H_{10}]/dt)_o$	$-(d[B_6H_{10}]/dt)_o^{corr}$ [c]	$(d[H_2]/dt)_o$	$(d[H_2]/dt)_o^{corr}$ [d]	$(d[B_5H_9]/dt)_o$	$(d[B_{10}H_{14}]/dt)_o$
	mmHg [b]			µmol m^{-3} s^{-1}						
372.7	1.75	3.51	0.0	1.1	4.0	3.3	2.2	1.5		
372.4	3.54	1.72	0.0	0.3	2.5	2.3	1.9	1.7		
371.8	3.51	3.46	0.0	2.7	5.8	5.0	3.6	2.9		
372.9	3.54	3.48	0.0	3.8	3.9	3.1	3.4	2.7		
372.3	3.43	7.02	0.0	~0	6.2	3.1	6.5	3.7		
371.8	7.00	3.48	0.0	1.0	3.6	2.8	5.5	4.8		
372.9	13.93	3.44	0.0	2.7	4.6	3.9	9.0	8.3		
398 ± 1	1.74	3.46	0.0	2.1	8.5	5.3	18.2	15.0		
398 ± 1	3.52	0.44	0.0	5.0	3.0	2.9	9.6	9.5		
398 ± 1	3.52	0.88	0.0	7.2	4.8	4.6	11.8	11.6		
398 ± 1	3.50	1.76	0.0	8.0	7.8	7.0	17.8	17.0		
398 ± 1	3.46	3.48	0.0	5.6	13.3	10.0	27.9	24.7		
398 ± 1	3.46	3.53	0.0	6.1	12.0	8.7	21.3	17.9		
398 ± 1	3.53	7.02	0.0	5.0	28.3	15.2	44.0	30.9		
398 ± 1	3.53	13.26	0.0	3.4	60.4	14.1	72.0	25.7		
398 ± 1	7.00	3.49	0.0	31.0	28.3	25.0	57.5	54.0		
398 ± 1	13.95	3.49	0.0	52.2	30.9	27.6	109.9	106.7		
408.1	1.77	3.50	0.0	10.3	36.0	30.6	63.3	57.9		0.8
408.1	3.47	1.76	0.0	23.7	21.3	19.9	50.2	48.8		4.3
408.1	3.51	1.76	15.0	14.2	24.3	22.9	66.5	65.1		2.8
408.1	3.50	3.50	0.0	18.2	31.1	25.7	68.2	62.8		5.8
408.1	3.47	3.47	15.0	17.3	37.5	32.2	66.8	61.5		2.6
408.1	3.48	6.95	0.0	17.8	56.6	35.3	141.9	120.6		3.9
408.1	3.46	7.00	15.0	18.6	59.6	38.0	137.3	115.7		4.1
408.1	7.04	3.53	0.0	55.7	45.0	39.5	112.8	107.3		10.6
408.1	7.04	3.55	15.0	45.9	38.6	33.0	107.4	101.8		9.1
408.1	10.45	3.48	0.0	61.1	69.7	64.4	196.0	190.7		9.9
408.1	10.48	3.53	15.1	72.5	66.0	60.6	210.9	205.5		16.3
408.1	13.92	3.51	0.0	75.4	115.3	109.9	256.5	251.1		21.6
408.1	13.92	3.54	15.0	74.2	89.5	84.0	246.1	240.6		19.3
423.7	1.77	3.49	0.0	10.8	31.2	18.6	40.6	28.0	0.7	3.7

Table 2 (*Continued*)

T/K	$p_o(B_2H_6)$	$p_o(B_6H_{10})$	$p_o(H_2)$	$-(d[B_2H_6]/dt)_o$	$-(d[B_6H_{10}]/dt)_o$	$-(d[B_6H_{10}]/dt)_o^{corr\ c}$	$(d[H_2]/dt)_o$	$(d[H_2]/dt)_o^{corr\ d}$	$(d[B_5H_9]/dt)_o$	$(d[B_{10}H_{14}]/dt)_o$
	mmHg [b]			µmol m^{-3} s^{-1}						
425.0	3.50	1.76	0.0	53.5	40.8	37.6	65.5	62.3	0.5	9.7
424.9	3.49	3.51	0.0	31.5	41.2	28.6	98.8	86.1	1.2	8.4
427.2	3.53	7.00	0.0	29.6	112.6	63.0	392.6	343.1	2.8	9.2
423.3	3.49	13.99	0.0	48.6			337.2	135.4		
425.2	7.02	3.49	0.0	116.3	70.4	58.0	185.4	173.0	2.6	22.2
423.0	7.02	3.94	16.9	124.6	99.6	84.3			2.2	25.3
423.5	13.94	3.49	0.0	284.9	208.3	195.7	472.9	460.3	10.3	51.7
423.0	14.0	3.50	10.0	351.2	172.7	160.6			10.8	63.3
423.0	14.0	3.50	16.8	314.0	301.8	289.7			10.5	71.0
422.5	20.6	3.46	0.0	341.5	203.1	190.8	630.7	618.3	26.7	90.0
437.1	1.75	3.49	0.0	28.7	127.2	102.6	42.2	17.4	1.0	12.5
437.1	3.52	1.73	0.0	114.9	99.7	93.7	192.4	186.2	2.3	17.2
437.0	3.48	3.49	0.0	111.8	82.6	57.9	183.1	158.4	6.5	21.6
436.5	3.50	6.95	0.0	71.8	190.7	93.0	315.9	218.8	3.7	22.5
438.4	3.51	14.00	0.0	68.6	453.1	57.3	591.3	195.0	17.1	26.8
437.9	6.97	3.46	0.0	317.3	238.9	214.7	472.3	447.7		41.0
437.4	14.0	3.46	0.0	641.6	422.2	398.0	1095	1072	28.6	110.0
471.1	3.51	3.49	0.0	602.1	550.2	454.8	1008	913.0		

[a] See appropriate footnote to Table 1.

[b] See appropriate footnote to Table 1.

[c] Initial rates corrected for B_6H_{10} consumed and H_2 produced in the second-order self-decomposition of B_6H_{10} (see [2] for relevant data).

[d] Rate too low to be measured accurately.

The values obtained for the consumption of B_2H_6 with respect to its own initial concentration were 1.46 ± 0.12 at 424 and 1.49 ± 0.15 at 437 K; i.e. the same as the established order of 3/2 for the gas-phase thermolysis of pure diborane [9] and strongly suggesting that B_2H_6 is undergoing the same initial rate-determining sequence of reactions leading to the production of the reactive intermediate $\{B_3H_7\}$:

$$B_2H_6 \rightleftharpoons 2\{BH_3\} \tag{1}$$

$$\{BH_3\} + B_2H_6 \overset{\text{slow}}{\rightleftharpoons} \{B_3H_9\} \rightleftharpoons \{B_3H_7\} + H_2 \tag{2}$$

As implied earlier, the order for the consumption of B_2H_6 with respect to the initial concentration of B_6H_{10} was found to be essentially zero, suggesting that the initial rate-determining sequence is followed by the rapid reaction of the intermediate $\{B_3H_7\}$ with B_6H_{10} to give higher boranes (see later). The order-plots for the consumption of B_6H_{10} and production of hydrogen were less informative, each showing curvature leading to increased orders at the higher temperatures. However, once it was realised that these data would include contributions from the competitive, second-order decomposition of B_6H_{10}, more meaningful results were forthcoming. Table 2 contains both the raw data and the initial rates corrected for this process. The order plots based on the corrected data now indicate zero-order dependence on the initial concentration of B_6H_{10}, consistent with the analysis of the B_2H_6 rate data. By contrast, there is a definite dependence on the initial concentration of B_2H_6; the order is less well defined, but is not inconsistent with the value of 3/2 determined from the more accurate B_2H_6-consumption data for which no corrections need to be applied. Rates of production of the minor products B_5H_9 and $B_{10}H_{14}$ have not been used in the kinetic analysis, but are given in Table 2 for completeness.

These results for the B_6H_{10}–B_2H_6 cothermolysis are therefore consistent with the rate equation, $\text{rate}_{\text{coth}} = k_{3/2,\text{coth}}[B_2H_6]^{3/2}$. Values for the 3/2-order rate constant at various temperatures have been evaluated from the B_2H_6-consumption, B_6H_{10}-consumption and H_2-production data (denoted $k_{3/2,B_2H_6}$, $k_{3/2,B_6H_{10}}$ and $k_{3/2,H_2}$, respectively), and listed in Table 3. If the working hypothesis is correct, the three values at any given temperature should agree, and this is in fact the case for $k_{3/2,B_2H_6}$ and $k_{3/2,B_6H_{10}}$. The $k_{3/2,H_2}$ values tend to be somewhat higher, but for reasons mentioned earlier this is perhaps not surprising.

The 3/2-order rate constants $k_{3/2,B_2H_6}$ for the cothermolysis are shown in the form of an Arrhenius plot, together with the data for the thermolysis of pure B_2H_6 in Fig. 1. It can be seen that the two sets of data do indeed lie close to the same line of best fit. The least-squares analysis of these data yields a value of 99.4 ± 2.5 kJ mol^{-1} for the activation energy, and a value of $e^{21.1 \pm 0.8}$ (ca. 1.5×10^9) $\text{m}^{3/2}$ $\text{mol}^{-1/2}$ s^{-1} for the pre-exponential factor. The corresponding values from the H_2-production data recorded in Table 1 are 92.5 ± 3.8 kJ mol^{-1} and $e^{19.7 \pm 1.1}$ (ca. 3.6×10^8) $\text{m}^{3/2}$ $\text{mol}^{-1/2}$ s^{-1}, and from the B_6H_{10}-consumption data, 82.9 ± 5.3 kJ mol^{-1} and $e^{16.5 \pm 1.5}$ (ca. 1.5×10^7) $\text{m}^{3/2}$ $\text{mol}^{-1/2}$ s^{-1}.

Included in Fig. 1 and indicated by open triangles, are data for two runs in which an excess of hydrogen was added to the B_6H_{10}–B_2H_6 cothermolysis. Interestingly, in marked contrast to the thermolysis of pure B_2H_6, the addition of hydrogen to the B_6H_{10}–B_2H_6 cothermolysis was found to have little effect on the rates (Table 2) or on the product distribution. The significance of this is discussed later.

Table 3
$^3/_2$-Order rate constants for the B_6H_{10}–B_2H_6 cothermolysis with and without added H_2 [a]

Added H_2 p/mmHg	T/K [b]	No. of runs [b]	$10^4 k_{3/2,B_2H_6}$	$10^4 k_{3/2,B_6H_{10}\text{corr.}}$	$10^4 k_{3/2,H_2\text{corr.}}$
			$\text{mol}^{-\frac{1}{2}}$ $\text{m}^{3/2}$ s^{-1}		
0.0	372 ± 1.7	7	0.30 ± 0.25	0.46 ± 0.52	0.40 ± 0.17
0.0	398 ± 1.0	10	1.2 ± 0.3	1.7 ± 0.8	4.3 ± 1.8
0.0	408 ± 0.5	7	3.6 ± 1.2	5.7 ± 4.6	14.0 ± 9.0
15.0	408 ± 0.5	7	3.3 ± 1.1	5.3 ± 3.3	15 ± 11
0.0	424 ± 1.4	8	7.0 ± 2.4	7.3 ± 3.6	21 ± 19
10.0	423 ± 0.5	1	9.1	4.2	
~17.0	423 ± 0.5	2	8.6	6.8	
0.0	437 ± 0.6	7	20 ± 4	16 ± 3	34 ± 11
0.0	471 ± 0.5	1	147	111	221

[a] Evaluated from the expressions $k_{3/2,B_2H_6} = -(d[B_2H_6]/dt)_o/[B_2H_6]_o^{3/2}$; $k_{3/2,B_6H_{10}\text{corr.}} = -d[B_6H_{10}]/dt)_o^{\text{corr.}}/[B_2H_6]_o^{3/2}$; and $k_{3/2,H_2\text{corr.}} = (d[H_2]/dt)_o^{\text{corr.}}/[B_2H_6]_o^{3/2}$; (see discussion and footnotes to Table 1 for definition of these corrected rates). Errors quoted are standard deviations. Initial rates for these various runs are given in Table 2.

[b] Errors in temperature measurement ca. ± 0.5 K; when values have been obtained from a series of runs, the error is the standard deviation from the mean value quoted.

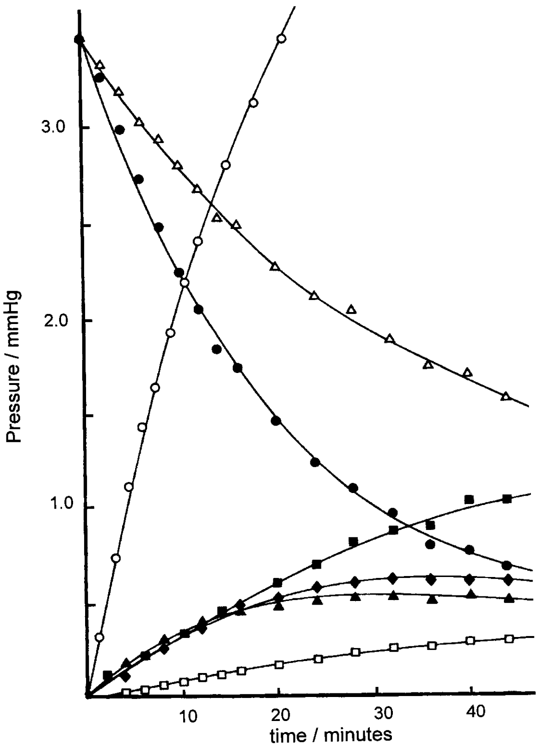

Fig. 3. Product analysis as a function of time for the cothermolysis at $T = 348.5$ K of B_6H_{10} (p_0 3.51 mmHg) with B_4H_{10} (p_0 3.51 mmHg): (●) B_4H_{10}, (△) B_6H_{10}, (○) H_2, (■) B_2H_6, (▲) B_5H_{11}, (◆) B_9H_{15}, (□) $B_{10}H_{14}$.

3.3. Cothermolysis of B_6H_{10} with B_4H_{10}

As B_4H_{10} is much less stable than B_2H_6, it was possible to study the B_6H_{10}–B_4H_{10} reaction over a range of temperatures, 40–90°C, at which pure B_6H_{10} does not undergo significant decomposition. This simplified the analysis of the data because it was not necessary to correct the reaction rates for the competitive self-decomposition of B_6H_{10}. A typical run at 348 K is shown in Fig. 3. Initial rates for all the reactions are given in Table 4. The cothermolysis showed parallels with the B_6H_{10}–B_2H_6 system in the sense that the rate of consumption of the co-reactant, B_4H_{10} in this case, was essentially the same as in the thermolysis of the pure gaseous compound over the temperature range studied [11,16] but the rate of decomposition of the B_6H_{10} was enhanced compared with that in the pure state [2]. The main products are seen to be H_2, B_2H_6, pentaboranes (mainly B_5H_{11} in the early stages) and B_9H_{15}; $B_{10}H_{14}$ builds up slowly and B_6H_{12} appears only in the later stages of the reaction.

Detailed kinetic analysis of the data indicated that the rate of consumption of B_4H_{10} was accurately first-order with respect to B_4H_{10} (i.e. the same as in the thermolysis of the pure compound) and zero order with respect to B_6H_{10}. The order determined from the production of H_2 was close to unity, 0.89 ± 0.07, with respect to the initial concentration of B_4H_{10}, but its rate of production was essentially independent of the initial

Table 4
Initial-rate data for cothermolysis of B_4H_{10} and B_6H_{10} with and without added H_2 [a]

T/K $^{\pm 0.5}$	$p_o(B_4H_{10})$	$p_o(B_6H_{10})$	$p_o(H_2)$	$-(d[B_4H_{10}]/dt)_o$	$-(d[B_6H_{10}]/dt)$	$(d[H_2]/dt)_o$	$(d[B_2H_6]/dt)_o$	$(d[B_5H_{11}]/dt)_o$
	mmHg [b]			μmol m^{-3} s^{-1}				
313.2	3.48	3.49	0.0	6.8	10.9	5.9	[c]	[c]
323.3	3.51	3.51	0.0	12.7	9.1	20.8	[c]	[c]
338.3	3.52	3.50	0.0	18.2	10.9	44.9	[c]	[c]
342.9	3.52	3.52	0.0	61.4	39.2	120.6	[c]	[c]
348.5	1.75	3.52	0.0	55.9	32.7	108.7	12.9	8.1
347.9	3.50	1.75	0.0	106.7	40.5	190.4	14.4	42.0
348.5	3.51	3.51	0.0	93.6	51.8	173.4	24.0	27.2
348.5	3.50	5.25	0.0	122.0	122.3	205.9	38.9	10.7
347.7	3.50	7.00	0.0	117.4	104.6	153.7	43.0	18.7
348.2	3.48	6.97	50.0	51.1	46.2	[c]	[c]	[c]
348.7	3.50	10.55	0.0	140.5	127.7	233.1	29.8	21.3
348.4	5.18	3.48	0.0	123.5	69.7	273.9	31.3	36.4
348.3	7.01	3.50	0.0	173.9	79.9	473.1	63.0	82.7
348.4	10.63	3.50	0.0	229.4	107.4	553.9	28.7	90.7
348.5	14.04	3.48	0.0	469.2	168.1	639.0	77.8	95.2
363.2	3.47	3.50	0.0	286.0	138.0	630.6	[c]	[c]

[a] See appropriate footnote to Table 1.

[b] See appropriate footnote to Table 1.

[c] Rate too low to be measured accurately.

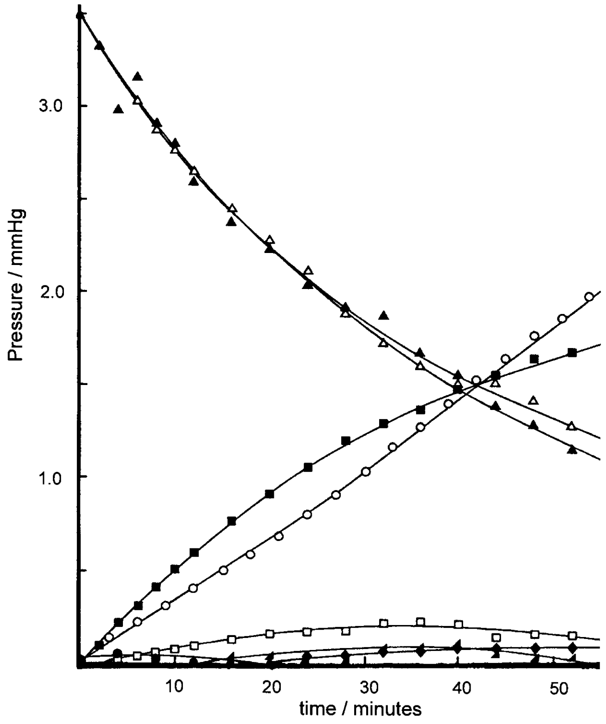

Fig. 4. Product analysis as a function of time for the cothermolysis at $T = 347.3$ K of B_6H_{10} (p_0 3.50 mmHg) with B_5H_{11} (p_0 3.50 mmHg): (▲) B_5H_{11}, (△) B_6H_{10}, (○) H_2, (■) B_2H_6, (●) B_4H_{10}, (▲) B_8H_{12}, (◆) B_9H_{15}, (□) $B_{10}H_{14}$.

concentration of B_6H_{10}. The activation energy for the decomposition of B_4H_{10} was found to be 88.4 ± 6.1 compared with 99.2 ± 0.8 kJ mol^{-1} for B_4H_{10} alone [11,16].

The effect of added H_2 on the reaction can be seen from the rates recorded in Table 4 for the pair of experiments in which the initial pressures of B_4H_{10} and B_6H_{10} were ca. 3.5 and 7.0 mmHg, respectively. The rate of decomposition of B_4H_{10} was reduced by half in the presence of H_2 at 50 mmHg . The retarding effect of added H_2 is therefore considerably less than that observed in the thermolysis of B_4H_{10} alone, but greater than that observed in the B_6H_{10}–B_2H_6 cothermolysis [16].

3.4. Cothermolysis of B_6H_{10} with B_5H_9 and with B_5H_{11}

When an equimolar mixture of B_6H_{10} and B_5H_9 was heated at 408 K, the partial pressure of the latter increased very slightly from ca. 3.5 to 3.7 mmHg over a period of 60 min, whereas the initial rate of decomposition of the B_6H_{10} was found to be the same as that observed [2] in the thermolysis of this borane alone. As B_5H_9 is known to be relatively stable in the gas phase at this temperature [17] the slight increase in its concentration can be attributed to the decomposition of B_6H_{10}, and it is apparent that little or no interaction occurs between these two boranes under the conditions employed.

By contrast, in the cothermolysis of B_6H_{10} and B_5H_{11} (Fig. 4) the two boranes were consumed rapidly, and at essentially identical initial rates. The main products were B_2H_6 and H_2, together with higher boranes B_8H_{12}, B_9H_{15} and $B_{10}H_{14}$ in smaller but significant amounts. Small amounts of B_4H_{10} were also observed in the early stages of the reaction. The rate of consumption of B_5H_{11} is comparable with that observed in the thermolysis of B_5H_{11} alone [18] but the rate of consumption of B_6H_{10} is increased by a massive 300/400-fold compared with its rate of decomposition when heated alone.

3.5. Mechanistic implications

In the cothermolysis reactions of B_6H_{10} separately with B_2H_6, B_4H_{10} and B_5H_{11} the rate of consumption of B_6H_{10} was considerably more rapid than in the thermolysis of B_6H_{10} alone, indicating clearly that interactions were occurring. In contrast, no reaction was observed between B_6H_{10} and B_5H_9 under the conditions studied. The 3/2 order observed in the B_6H_{10}–B_2H_6 reaction suggests that B_6H_{10} must react with the $\{B_3H_7\}$ intermediate formed from B_2H_6, and not with either B_2H_6 itself or with $\{BH_3\}$.

$$\{B_3H_7\} + B_6H_{10} \rightarrow B_9H_{15} + H_2 \qquad (3)$$

Such a step has been proposed in the past without direct evidence [19] and it has been shown that B_6H_{10} reacts with [10] B_3H_7.THF at 273 K in the presence of BF_3 to give a labelled B_9H_{15} [8a]. Step (3) presumably competes successfully with the reaction of $\{B_3H_7\}$ with B_2H_6 that is thought to lead to B_4H_{10} in the absence of B_6H_{10} [20]. We considered the possibility that the B_2H_6 decomposition might proceed as far as the production of $\{B_4H_8\}$ [reactions (4) and (5)] before the interaction with B_6H_{10} occurs,

$$\{B_3H_7\} + B_2H_6 \rightarrow B_4H_{10} + \{BH_3\} \qquad (4)$$

$$B_4H_{10} \rightleftharpoons \{B_4H_8\} + H_2 \qquad (5)$$

but the lack of inhibition in the presence of a large excess of added H_2 demonstrates that B_6H_{10} must react very rapidly with $\{B_3H_7\}$ [(reaction (3)] before the latter can be re-converted to B_2H_6 by reaction (2).

In the B_6H_{10}–B_2H_6 cothermolysis the temperature is too high for B_9H_{15} to survive, and it must react further to generate the substantial amounts of $B_{10}H_{14}$ that are observed. This reaction is known to occur, but isotope studies have shown that it probably takes place in a two-stage process involving B_8H_{12} and $\{B_9H_{13}\}$ as intermediates [21]. In the B_6H_{10}–B_4H_{10} and B_6H_{10}–B_5H_{11} reactions, the temperatures are low enough to allow B_9H_{15} to survive, and it is actually observed as an important product in the early stages of these reactions. A similar result has been observed in the reaction at even lower temperatures between the unstable adduct B_4H_8CO and B_6H_{10} [22] and it seems likely that the reaction involving $\{B_4H_8\}$ is responsible in each case.

$$\{B_4H_8\} + B_6H_{10} \rightarrow B_9H_{15} + \{BH_3\} \tag{6}$$

In both the B_6H_{10}–B_2H_6 and B_6H_{10}–B_4H_{10} cothermolyses the production of B_9H_{15} [reactions (3) and (6), respectively] is presumed to be in competition with the reaction leading to the formation of B_5H_{11} [reaction (7)]. Accordingly, as observed,

$$\{B_4H_8\} + B_4H_{10} \rightarrow B_5H_{11} + \{B_3H_7\} \tag{7}$$

the latter is produced at a substantially reduced rate compared with its rate of formation in the thermolysis reactions of B_2H_6 and B_4H_{10} alone.

The B_6H_{10}–B_5H_{11} system has not been studied in depth, but the results indicate that the kinetics of this reaction are also governed by the proposed [18] rate-determining step in the decomposition of B_5H_{11}, namely the elimination of $\{BH_3\}$ to give $\{B_4H_8\}$. The observation that the two reactants are consumed at the same rate suggests that the $\{B_4H_8\}$ is mopped up in a very efficient reaction with B_6H_{10}. The substantial production of B_2H_6 can be understood in terms of the high concentrations of $\{BH_3\}$ expected to be produced from the rate-determining dissociation of B_5H_{11} and from the dissociation of the B_9H_{15}.

These results demonstrate in a very striking way the strong affinity that exists between B_6H_{10} and the intermediates $\{B_3H_7\}$ and $\{B_4H_8\}$. In view of the fact that both the B_2H_6 and B_4H_{10} decompositions are retarded by the presence of added H_2, the lack of inhibition in the B_6H_{10}–B_2H_6–H_2 system, even in the presence of a 10-fold excess of added H_2, demonstrates that B_6H_{10} is particularly effective in its competition for $\{B_3H_7\}$. The results lend quantitative support to Schaeffer's early suggestion that B_6H_{10} plays a key role in the production of higher boranes in thermolytic reactions of smaller binary boranes.

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