Influence of Added Hydrogen on the Kinetics and Mechanism of Thermal Decomposition of Tetraborane(10) and of Pentaborane(11) in the Gas Phase *

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The effects of added hydrogen on the kinetics of the first-order thermal decomposition of the two *arachno* species tetraborane(10) and pentaborane(11) have been studied in detail by a mass-spectrometric method. In the case of B_4H_{10}, the order and activation energy were unaltered, but the reaction rate was retarded and there was a marked change in product distribution: the percentage yield of B_5H_{11} remained the same, but B_2H_6 was formed in preference to B_5H_9, B_6H_{12}, $B_{10}H_{14}$, and involatile solids. These results provide cogent new evidence that B_4H_{10} decomposes *via* the single rate-determining step (i), but raise doubts about the validity of subsequent steps in the

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

previously proposed mechanism. In the thermolysis of B_5H_{11} there was a dramatic change in product distribution, but the order, activation energy, *and* initial rate of disappearance of B_5H_{11} were all unaffected by the presence of the added H_2. These results establish for the first time that the so-called 'equilibrium' (ii) proceeds in the forward direction *via* the rate-determining

$$B_5H_{11} + H_2 \rightleftharpoons B_4H_{10} + \tfrac{1}{2}B_2H_6 \qquad \text{(ii)}$$

dissociation (iii), followed by the rapid reactions (−i) and (iv). They also imply that in the thermolysis

$$B_5H_{11} \longrightarrow \{B_4H_8\} + \{BH_3\} \qquad \text{(iii)}$$

$$2\{BH_3\} \longrightarrow B_2H_6 \qquad \text{(iv)}$$

of B_5H_{11} in the absence of added H_2 the reactive intermediate $\{B_4H_8\}$ reacts subsequently with itself and is not consumed by reaction with B_5H_{11}.

arachno-Tetraborane, B_4H_{10}, is a highly reactive gas which readily interconverts to other boranes above about 40 °C. There has been uncertainty in the literature about almost all aspects of its thermolysis, but we have recently resolved many of these problems by means of a detailed mass-spectrometric study.[1] At the centre of these discussions has been the question of the precise nature of the initial step. Our earlier reports have reviewed the background to this subject, and have outlined our reasons for believing that the reaction proceeds *via* the (reversible) unimolecular elimination of H_2 from B_4H_{10} [reaction (1)], rather than the elimination of $\{BH_3\}$ or, as was

$$B_4H_{10} \rightleftharpoons \{B_4H_8\} + H_2 \qquad (1)$$

originally suggested,[2] by a combination of both routes. The reactive intermediate $\{B_4H_8\}$ is then thought to react rapidly with B_4H_{10} to give B_5H_{11} as the main volatile borane product [equation (2)]. On this basis an excess of added H_2 should

$$\{B_4H_8\} + B_4H_{10} \longrightarrow B_5H_{11} + \{B_3H_7\} \qquad (2)$$

inhibit the decomposition of B_4H_{10} and alter the product distribution. There are in fact qualitative indications to this effect in the literature,[2,3] but we wished to put these observations on a more quantitative basis. In particular we wished to determine the Arrhenius parameters for the thermolysis of B_4H_{10} in the presence of added H_2, to establish whether the suppression of reaction (1) would alter the observed activation energy, and thereby reveal the presence of any competing rate-determining step.

We have recently completed a detailed kinetic study of the thermolysis of B_5H_{11} in the absence of added H_2 which, by contrast, strongly suggests that the initial step for this borane involves the rate-determining release of $\{BH_3\}$, followed by rapid dimerization of the latter to give B_2H_6 with approximately 100% efficiency [equations (3) and (4)].[4] The precise fate

$$B_5H_{11} \longrightarrow \{B_4H_8\} + \{BH_3\} \qquad (3)$$

$$2\{BH_3\} \rightleftharpoons B_2H_6 \qquad (4)$$

of the reactive intermediate $\{B_4H_8\}$ was not established in detail, and it was hoped, again, that experiments with added H_2 would give further insights into the processes occurring. It has often been suggested[2,3,5] that B_5H_{11} and B_4H_{10} are interconvertible in the presence of H_2, according to the 'equilibrium' (5). However, it was not clear whether the forward reaction

$$B_5H_{11} + H_2 \rightleftharpoons B_4H_{10} + \tfrac{1}{2}B_2H_6 \qquad (5)$$

occurred as a single step (*i.e.* BH abstraction by H_2 from B_5H_{11}) or as a combination of reactions (3), (4), and (−1).

To resolve these various problems we have carried out detailed studies of the effects of added H_2 on the kinetics of thermal decomposition of both B_4H_{10} and B_5H_{11} over a range

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* *Non-S.I. unit employed:* mmHg ≈ 133 Pa.

Table 1. Initial-rate data for thermolysis of B_4H_{10} in the presence of added H_2[a]

T/K ($\pm$0.5)	$p_0(B_4H_{10})$/ mmHg	$10[B_4H_{10}]_0$/ mol m^{-3}	$p_0(H_2)$/ mmHg	$10[H_2]_0$/ mol m^{-3}	$-10^6 \times (d[B_4H_{10}]/dt)_0$	$10^6 \times (d[H_2]/dt)_0$[b]	$10^6 \times (d[B_2H_6]/dt)_0$	$10^6 \times (d[B_5H_{11}]/dt)_0$
					mol m^{-3} s^{-1}			
323.3	3.51	1.74	20.0	9.9	1.7		0.3	0.5
332.9	3.48	1.68	19.9	9.6	5.6		0.7	1.4
348.2	3.49	1.61	19.9	9.2	24.1		3.8	17.9
362.1	1.78	0.79	50.0	22.1	47.6		12.9	12.7
362.8	3.51	1.55	0.0	0.0	344		17.5	169
361.8	3.51	1.55	50.1	22.2	60.8		20.2	39.4
361.8	5.30	2.35	50.0	22.2	88.6		24.6	51.1
361.7	7.05	3.13	50.0	22.2	128		37.0	59.5
362.1	13.5	5.98	49.9	22.1	274		91.4	151
363.5	3.50	1.54	20.1	8.9	91.9	123	14.1	49.6
373.1	3.49	1.50	20.1	8.6	212	462	31.8	125
383.7	3.49	1.46	20.1	8.4	476	794	89.3	288

[a] Systematic errors in pressure measurements *ca.* ±1%, and in initial rates *ca.* 5%. [b] Data for H_2 not recorded for most runs because of large background from added H_2.

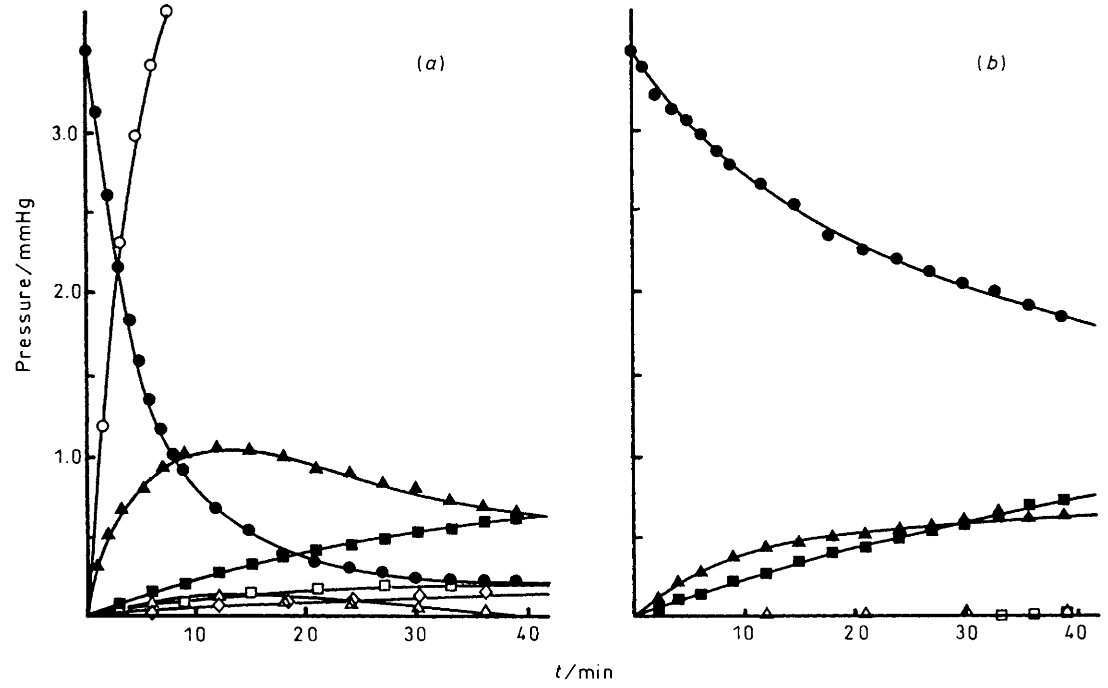

Figure 1. Reaction profiles for the thermolysis of (*a*) B_4H_{10} (p_0 = 3.51 mmHg) at 89.7 °C and (*b*) B_4H_{10} (p_0 = 3.51 mmHg) and H_2 (p_0 = 50.1 mmHg) at 88.7 °C, showing the influence of added hydrogen: (○) H_2, (●) B_4H_{10}, (▲) B_5H_{11}, (■) B_2H_6, (△) B_6H_{12}, (□) $B_{10}H_{14}$, and (◇) B_5H_9. Data for H_2 were not recorded in (*b*) because of the large initial background from added H_2

of temperature and pressure. Some preliminary findings have been referred to elsewhere,[6] but we now report a full account of the work.

Experimental

The quantitative mass-spectrometric techniques used in this work have been described in detail elsewhere.[1,7] All thermolyses were carried out in 'conditioned,' spherical Pyrex bulbs 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.[4] From the results of our previous work with B_4H_{10}[1] and B_5H_{11}[4] it seems reasonable to conclude that, under the present experimental conditions, we are dealing with homogeneous gas-phase reactions: both of the decompositions were shown to be unaffected by 'conditioned' Pyrex surfaces, and it is most unlikely that the presence of added H_2 would induce any heterogeneous component.

The boranes were prepared by the methods of Shore and co-workers,[8,9] and handled throughout using standard grease-free vacuum-line techniques. Purification was achieved by trap-to-trap fractionation, followed where necessary by fractionation on a low-temperature column.[4]

Results

Reaction Profiles and Initial-rate Data.—Typical reaction profiles for the thermolysis of B_4H_{10} alone and in the presence of *ca.* 50 mmHg added H_2 are compared in Figure 1, and similar results for B_5H_{11} are shown in Figure 2. These particular

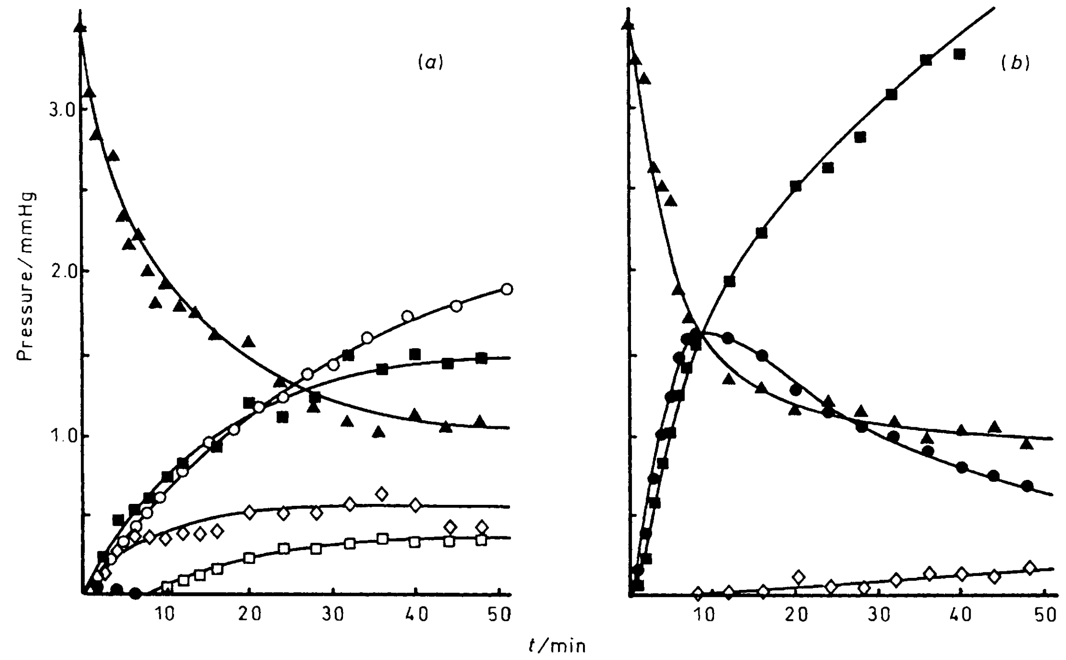

Figure 2. Reaction profiles for the thermolysis of (*a*) B_5H_{11} (p_0 = 3.52 mmHg) at 99.9 °C (data from ref. 4) and (*b*) B_5H_{11} (p_0 = 3.53 mmHg) and H_2 (49.9 mmHg) at 100.1 °C, showing the influence of added hydrogen on the thermolysis of B_5H_{11}: symbols as in Figure 1

Table 2. First-order rate constants for the thermolysis of B_4H_{10} alone and in the presence of added H_2[a]

		$10^6k_1/s^{-1}$		
Added H_2 p/mmHg	T/K ($\pm$0.5)	From B_4H_{10} consumption	From B_2H_6 production	From B_5H_{11} production
0.0	362.8	2 217	113	1 090
20.0	323.3	9.8	1.7	2.9
19.9	332.9	33.3	4.2	8.3
19.9	348.2	150	23.6	109
20.1	363.5	597	91.6	322
20.1	373.1	1 415	212	835
20.1	383.7	3 260	617	1 969
50.0	361.8	448 ± 82[b]	134 ± 22[b]	215 ± 36[b]

[a] Evaluated from the expressions k_1(from B_4H_{10} consumption) = $-(d[B_4H_{10}]/dt)_0/[B_4H_{10}]_0$, k_1(from B_2H_6 production) = $(d[B_2H_6]/dt)_0/[B_4H_{10}]_0$, and k_1(from B_5H_{11} production) = $(d[B_5H_{11}]/dt)_0/[B_4H_{10}]_0$. [b] Mean values from five runs at this temperature (see Table 1); errors quoted are standard deviations.

B_4H_{10} runs were performed at *ca.* 90 °C and the B_5H_{11} runs at *ca.* 100 °C, but the initial pressures of the boranes were the same (*ca.* 3.5 mmHg) in each case. A complete set of reaction profiles for the numerous thermolyses performed in this work can be found elsewhere.[10] Initial rates, determined by the tangent method, are listed in Tables 1—3 together with the derived first-order rate constants.

From Figure 1 it is clear that the thermal decomposition of B_4H_{10} is substantially inhibited by the presence of added H_2, and that there is a dramatic change in product distribution. After 6 min in the thermolysis of B_4H_{10} alone [Figure 1(*a*)] the distribution of boron amongst the various products is 49% as B_5H_{11}, 8% as $B_{10}H_{14}$, 6% as B_6H_{12}, 4% as B_2H_6, 2% as B_5H_9, and 31% as involatile solids (from mass-balance calculations). In contrast, in the presence of added H_2 [Figure 1(*b*)] the distribution of boron is 59% as B_5H_{11}, 34% as B_2H_6, 1% as B_5H_9, and <6% as solids. However, from the results in Table 1, it is particularly interesting that on a molar basis the relative rates of production of B_5H_{11} ($r_{i,B_5H_{11}}$) to consumption of B_4H_{10} ($r_{i,B_4H_{10}}$) in the presence of H_2 are unaltered from those of the thermolysis of B_4H_{10} alone. For the six runs carried out with 20 mmHg added H_2 the average value of the ratio $r_{i,B_5H_{11}}/r_{i,B_4H_{10}}$ is 0.50 ± 0.18, and for the five runs with 50 mmHg added H_2 the average is 0.50 ± 0.13. These values are in excellent agreement with the value of 0.49 obtained in this study, and the values in the range 0.4—0.5 reported in our earlier, more detailed, study of B_4H_{10} alone.[1] On the other hand, the ratio $r_{i,B_2H_6}/r_{i,B_4H_{10}}$ is found to increase systematically from 0.05 in the B_4H_{10}-alone thermolysis, through 0.16 ± 0.02 in the runs with 20 mmHg added H_2, to 0.30 ± 0.03 in the presence of 50 mmHg added H_2.

Turning now to the thermolysis of B_5H_{11}, it can be seen from the typical reaction profile in Figure 2 that in this case also there is a marked change in product formation when excess of H_2 is added to the system. The compound B_4H_{10}, which is virtually absent in the thermolysis of B_5H_{11} alone, is now the main product, its rate of formation in the initial stages being almost equal to the rate of consumption of B_5H_{11}. However, its concentration reaches a maximum, after about 10 min in this particular thermolysis (100 °C), and then drops steadily as the reaction proceeds. The only other volatile borane produced in the early stages, B_2H_6, appears at a somewhat faster rate than it does when H_2 is not added initially, and from mass-balance calculations it is apparent that, after 3 min, some 30% of the boron from the B_5H_{11} consumed is present as B_2H_6. Thereafter, its concentration continues to rise steadily throughout the thermolysis. Hydrogen is the only other volatile species produced initially, but its concentration has not been recorded in these experiments because of difficulties of obtaining accurate data when a large added background is present initially. Formation of all other boranes, including B_5H_9, B_6H_{12}, $B_{10}H_{14}$, and involatile solid, is almost entirely suppressed by the presence of an excess of added H_2, at least in the early stages of the reaction. Despite these major effects on the product

Table 3. Initial-rate data and first-order rate constants for thermolysis of B_5H_{11} in the presence of added H_2[a]

T/K ($\pm$0.5)	$p_0(B_5H_{11})$/ mmHg	$10[B_5H_{11}]_0$/ mol m^{-3}	$p_0(H_2)$/ mmHg	$10[H_2]_0$/ mol m^{-3}	$-10^6 \times$ $(d[B_5H_{11}]/dt)_0$/ mol m^{-3} s^{-1}	$10^3k_{1,B_5H_{11}}$[b]/s^{-1}
333.5	3.52	1.69	49.9	24.0	9.4	0.055
348.2	3.51	1.62	50.1	23.1	23.0	0.142
373.2	3.53	1.52	49.9	21.5	198	1.30
398.3	3.53	1.42	49.9	20.1	748	5.26

[a] See footnotes to Table 1. [b] Evaluated from the expression $k_{1,B_5H_{11}} = -(d[B_5H_{11}]/dt)_0/[B_5H_{11}]_0$.

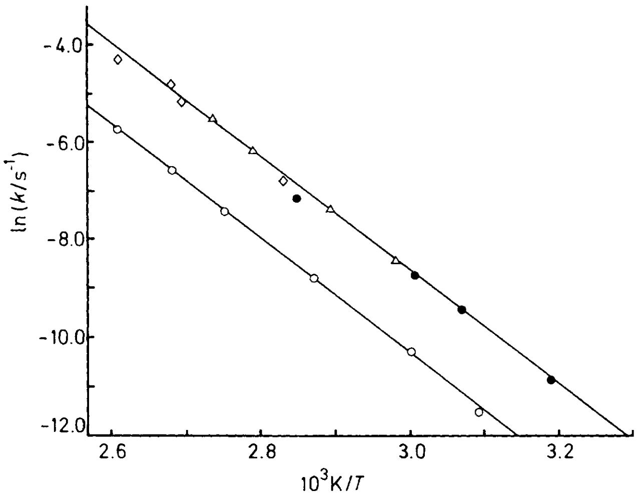

Figure 3. Arrhenius plots for the thermolysis of B_4H_{10} alone (●),[1] in cothermolysis with B_2H_6 (△)[5a] and CO (◇),[11] and in the presence of 20 mmHg added H_2 (○, this work)

distribution it is remarkable that the initial rate of consumption of B_5H_{11} is virtually unaltered by the presence of a 14-fold excess of added H_2. This specific point is considered in more detail in the following section, and is later shown to have important mechanistic implications.

Reaction Order and Arrhenius Parameters.—The initial-rate data from Table 1 for the B_4H_{10}/H_2 cothermolysis at *ca.* 90 °C when plotted in the form of log(initial rate) *versus* log(initial concentration) give slopes that in each case are very close to unity, indicating that the consumption of B_4H_{10} and the production of both B_2H_6 and B_5H_{11} are all first order with respect to the initial concentration of B_4H_{10}. The actual slopes of the lines of best fit are 0.88 ± 0.05 for consumption of B_4H_{10}, 0.95 ± 0.14 for the production of B_2H_6, and 1.10 ± 0.11 for the production of B_5H_{11}. Order plots of this type have not been obtained for the B_5H_{11}/H_2 cothermolysis, but as will become apparent this reaction is also first order with respect to the initial concentration of B_5H_{11} but zero order with respect to the concentration of hydrogen.

The first-order rate constants given in Tables 2 and 3 for the consumption of B_4H_{10} and B_5H_{11} in their respective cothermolyses with H_2 are recorded in the form of Arrhenius plots in Figures 3 and 4. Figure 3 also includes, for comparison (upper line), data for the thermolysis of B_4H_{10} alone,[1] and in cothermolysis with B_2H_6[5a] and CO.[11] It is at once apparent that the presence of 20 mmHg added H_2 leads to a consistent diminution (by a factor of *ca.* 5) in the rate of decomposition of B_4H_{10}, but leaves the activation energy unaltered. Essentially similar values for the activation energy were obtained from plots based on the rate constants for the production of B_2H_6 and B_5H_{11} (Table 2). The Arrhenius data for B_5H_{11} in Figure 4 demonstrate the point made earlier that the intial rates are unaltered by the presence of a 14-fold excess of added H_2. The activation energies are therefore essentially the same as in the thermolysis of B_5H_{11} alone, despite the fact that the observed product distributions are quite different. The numerical values of the activation energies and pre-exponential factors determined, respectively, from the slopes and intercepts of these plots are gathered together in Table 4 with values obtained in our earlier work for the thermolyses of B_4H_{10}[1] and B_5H_{11}[4] in the absence of added H_2. The apparent difference in the activation energies for the thermolysis of B_5H_{11} alone and in the presence of 50 mmHg added H_2 is within the error limits defined by the standard deviations, and is therefore not thought to be significant. This view was confirmed by the results of an additional series of experiments carried out with smaller initial pressures of B_5H_{11} (1 mmHg) and H_2 (10 mmHg), so that initial

Table 4. Arrhenius parameters for the thermolysis of B_4H_{10} and B_5H_{11}, alone and in the presence of added H_2

System	Activation energy, E_a/kJ mol^{-1}	Pre-exponential factor, A/s^{-1}	Ref.
B_4H_{10}	99.2 ± 0.8	$e^{27.1 \pm 0.3}$(*ca.* 6.0×10^{11})	1
$B_4H_{10} + H_2$[a]	98.4 ± 1.4	$e^{25.1 \pm 0.5}$(*ca.* 8.0×10^{10})	This work
B_5H_{11}	72.6 ± 2.4	$e^{16.4 \pm 0.8}$(*ca.* 1.3×10^{7})	4
$B_5H_{11} + H_2$[b]	80.1 ± 5.4	$e^{19.0 \pm 1.9}$(*ca.* 1.8×10^{8})	This work

[a] $p_0(H_2)$ = 20 mmHg, ratio H_2/B_4H_{10} = 5.73. [b] $p_0(H_2)$ = 50 mmHg, ratio H_2/B_5H_{11} = 14.2.

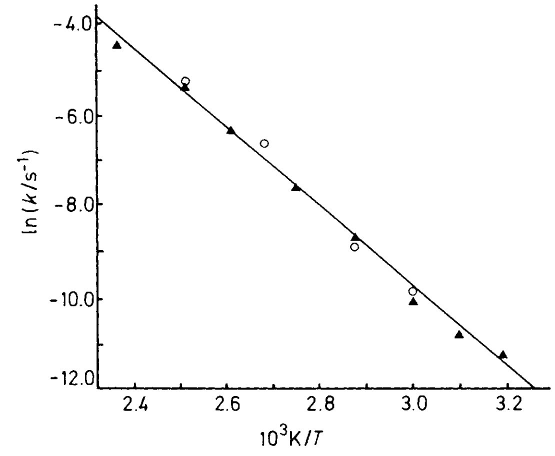

Figure 4. Arrhenius plots for the thermolysis of B_5H_{11} alone (▲)[4] and in the presence of 50 mmHg added H_2 (○, this work). The line drawn through the data is the least-squares best fit to the data for the thermolysis of B_5H_{11} alone; the least-squares best fit to the data for the B_5H_{11}/H_2 cothermolysis yields a slightly greater activation energy, but the difference is not thought to be significant (see text)

rates of production of H_2 could be monitored without causing saturation problems (see Table 1, footnote *b*). These measurements are not discussed in detail here because the initial rates are in general less precisely defined, owing to the smaller amounts of material involved. However, despite somewhat greater scatter in the data, the rate constants for both consumption of B_5H_{11} and production of H_2 were generally in good agreement with the Arrhenius data for the thermolysis of B_5H_{11} alone.

Discussion

Cothermolysis of Tetraborane(10) *and Hydrogen.*—As mentioned in the Introduction, our recent results on the thermolysis of B_4H_{10} alone have been interpreted in terms of a mechanism involving the initial rate-determining elimination of H_2 to produce the short-lived reactive intermediate $\{B_4H_8\}$ [reaction (1)], followed by the rapid reaction of this species with B_4H_{10} to give B_5H_{11} and $\{B_3H_7\}$ [reaction (2)].[1] The changes in product distribution observed in the present study, when H_2 is added initially to the thermolysis of B_4H_{10}, are entirely consistent with this mechanism. Thus, inhibition is accounted for by the increased importance of the back reaction (−1), which is in competition with reaction (2), but the percentage yield of B_5H_{11} is expected to be unaltered, as observed experimentally. Moreover, the relative increase in the rate of formation of B_2H_6 can be explained by the increased importance of reactions (6), (7), and (4).

$$\{B_3H_7\} + H_2 \rightleftharpoons \{B_3H_9\} \quad (6)$$

$$\{B_3H_9\} \rightleftharpoons B_2H_6 + \{BH_3\} \quad (7)$$

These three steps are the reverse of the accepted sequence by which B_2H_6 is thought to decompose,[12] and are seen to channel the reactive species $\{B_3H_7\}$ into the formation of this volatile borane at the expense of involatile 'polymer' which may otherwise be formed *via* reactions such as (8)[1] and/or (9).[8] The virtual

$$2\{B_3H_7\} \longrightarrow \{\text{`}B_6H_{14-2m}\text{'}\}(\text{polymerizes}) + mH_2 \quad (8)$$

$$2\{B_3H_7\} \longrightarrow B_4H_{10} + \{\text{`}B_2H_4\text{'}\}(\text{polymerizes}) \quad (9)$$

absence of B_6H_{12} can also be understood in terms of the competitive removal by added H_2 of the reactive intermediates $\{B_3H_7\}$ and $\{B_4H_8\}$ *via* reactions (6) and (−1) rather than their participation in reactions (10)—(12) which could otherwise arise in the normal thermolysis of B_4H_{10} (though there are reasons[1] why the last of these is less likely).

$$\{B_3H_7\} + B_5H_{11} \longrightarrow B_6H_{12} + B_2H_6 \quad (10)$$

$$\{B_4H_8\} + B_5H_{11} \longrightarrow B_6H_{12} + \{B_3H_7\} \quad (11)$$

$$2\{B_3H_7\} \longrightarrow B_6H_{12} + H_2 \quad (12)$$

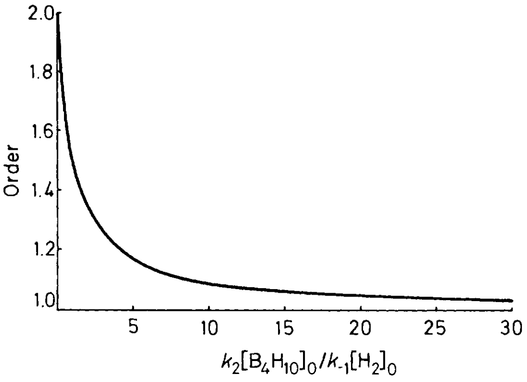

Figure 5. Theoretical dependence of reaction order* on the ratio $k_2[B_4H_{10}]_0/k_{-1}[H_2]_0$ for the proposed three-step mechanism in the thermolysis of B_4H_{10} in the presence of added H_2. This plot is based on equation (13), and assumes that steps (1), (−1), and (2) are the only important reactions involving B_4H_{10} and $\{B_4H_8\}$ in the initial stages (*This refers to the order for the consumption of B_4H_{10} with respect to the concentration of B_4H_{10}.)

However, all is not well with this mechanism since there appears to be an inconsistency between the magnitude of the observed retardation and the experimentally observed reaction order for the decomposition of B_4H_{10} in the presence of excess of added H_2. Thus, by application of 'steady-state' arguments, it can be shown that the expected rate of consumption of B_4H_{10} is given by equation (13), and the expected order by equation (14). From the form of equation (14) it follows that the order would be 2, if $k_{-1}[H_2]_0 \gg k_2[B_4H_{10}]_0$. However if the rates of reactions (−1) and (2) approach one another (*i.e.* $k_{-1}[H_2]_0 = k_2[B_4H_{10}]_0$) the expected order drops to 3/2, and as the relative rate of (2) increases further the order approaches unity. This is illustrated in Figure 5, which shows the calculated dependence of the reaction order on the ratio $k_2[B_4H_{10}]_0/k_{-1}[H_2]_0$ for the three-step mechanism (1), (−1), and (2). Equations (13) and (14) both assume of course that subsequent to the rate-determining step there are no other significant reactions involving B_4H_{10} and $\{B_4H_8\}$ in the 'initial' stages of the reaction. Now, on the basis of equation (13), the *ca.* 5-fold reduction observed in the inital rate in the presence of 20 mmHg added H_2 implies a value of *ca.* 0.7 for the rate-constant ratio k_{-1}/k_2, and from equation (14) this leads to a predicted order (in the presence of 50 mmHg added H_2) of *ca.* 1.9, which disagrees with the values of *ca.* 1 observed experimentally. It therefore appears that the mechanism referred to above is either oversimplified or incorrect.

$$\frac{-d[B_4H_{10}]}{dt} = \frac{2k_1k_2[B_4H_{10}]^2}{k_{-1}[H_2] + k_2[B_4H_{10}]} \quad (13)$$

$$\text{Order} = \frac{d\log(d[B_4H_{10}]/dt)_0}{d\log[B_4H_{10}]_0} = 2 - \frac{k_2[B_4H_{10}]_0}{k_{-1}[H_2]_0 + k_2[B_4H_{10}]_0} \quad (14)$$

In seeking an alternative explanation, it seems most unlikely that the proposed initial step [reaction (1)] is incorrect. The evidence in favour of the elimination of H_2 in the absence of added H_2 is now overwhelming,[1] and the results in Figure 3, from which it is apparent that the activation energy remains unaltered though the absolute rate of decomposition has diminished by a factor of *ca.* 5, provide cogent additional evidence that this is also the case when excess of added H_2 is present. If a concurrent rate-determining step such as release of BH_3 also occurred, suppression of (1) would favour this presumed concurrent step and this could explain the persistence of first-order kinetics in the presence of added H_2. However, it is not obvious that such a mechanism would leave the percentage yield of B_5H_{11} unchanged and, in any case, suppression of (1) would inevitably alter the observed activation energy towards that of the alternative route; it is most unlikely that this would fortuitously be identical to that of (1). It is also worth noting that there is no evidence in this work, kinetic or otherwise, for the existence of the hypothetical transient species $\{B_4H_{12}\}$,[13] whose formation *via* the direct interaction of B_4H_{10} and H_2 might have been expected to be favoured under the present experimental conditions.

It is possible that the second step involves the mutual interaction of the short-lived intermediate species $\{B_4H_8\}$ to give B_5H_{11} and the reactive intermediate $\{B_3H_5\}$ [reaction (15)].

$$2\{B_4H_8\} \longrightarrow B_5H_{11} + \{\text{'}B_3H_5\text{'}\}\ \text{(polymerizes)} \quad (15)$$

Such a reaction has been invoked by Shore and co-workers[8] in a different context to account for the high-yield synthesis of B_5H_{11} in solution at low temperature. In the absence of H_2 the $\{\text{'}B_3H_5\text{'}\}$ could polymerize, as indicated, but in the presence of added H_2 it could be converted *via* $\{B_3H_7\}$ into $\{B_3H_9\}$ and subsequently *via* reactions (7) and (4) to B_2H_6. This alternative mechanism is more difficult to analyse on the basis of 'steady-state' considerations of the type discussed earlier. It can be shown that under conditions where the rate of the back reaction (-1) is very much faster than that of the second step [reaction (15)], then the expected order is again 2. However, it is not obvious whether this situation prevails in the present experiments, because the form of the expression for the rate of consumption of B_4H_{10} does not readily yield a value for the rate-constant ratio k_{-1}/k_2 from the observed retardation. Further work is clearly required in this area.

Cothermolysis of Pentaborane(11) *and Hydrogen.*—The observation that the initial rate of decomposition of B_5H_{11} remains unaltered in the presence of a 14-fold excess of added H_2 (see Figures 2 and 4) has major mechanistic implications. Taken together with the dramatically altered product distribution, this new result enables important conclusions to be drawn about the detailed sequence of events involved in the thermolysis of B_5H_{11}, both in the presence of added H_2 and alone. As a result, several long-standing areas of uncertainty can be resolved.

Thus, it is at once clear that the forward reaction (5) does not occur in a single step by the direct abstraction of a BH group from B_5H_{11} by H_2. If this were the case, the reaction rate and activation energy would undoubtedly be different from the values obtained in the absence of added H_2. The alternative mechanism, involving prior dissociation of the B_5H_{11} *via* reaction (3) is therefore preferred. Further evidence in favour of this route is manifest in the product analysis. In the *initial* stages of the reaction, the rate of production of B_4H_{10} is seen to match very closely the rate of consumption of B_5H_{11} [*e.g.* Figure 2(*b*)], which is precisely as one would expect if reaction (-1) were *ca.* 100% effective. Likewise the rapid formation of B_2H_6 is readily explained by the recombination *via* (4) of the $\{BH_3\}$ fragments produced in (3). On the basis of this simple three-step mechanism [(3), (4), and (-1)], B_2H_6 is expected to be formed at half the rate of B_4H_{10}. Close inspection of Figure 2(*b*) reveals that in the first minute or two this is probably the case. However, after this initial period the two species appear at approximately the same rate, presumably because the B_4H_{10} is itself decomposing along the lines already outlined, yielding further B_2H_6 as a major product.

As suggested at the beginning of this section, the new results provided by this first systematic quantitative study of the effect of added H_2 on the kinetics of the thermal decomposition of B_5H_{11} have important implications with regard to the thermolysis of B_5H_{11} on its own. In the absence of added H_2, reaction (-1) is no longer important and the reactive intermediate $\{B_4H_8\}$ must therefore be consumed *via* an alternative route. In our recent study of this system,[4] several options were considered but it was not possible, on the basis of the evidence available at that time, to decide between them. However, in the light of the new evidence that the rate of consumption of B_5H_{11} is unaltered when excess of H_2 is present, it is possible to rule out several potential steps involving interaction of $\{B_4H_8\}$ with B_5H_{11} itself. The possibility of straight exchange of BH_3 between B_5H_{11} and $\{B_4H_8\}$ according to equation (16) cannot

$$\{B_4H_8\} + B_5H_{11} \longrightarrow B_5H_{11} + \{B_4H_8\} \quad (16)$$

of course be ruled out on the basis of these experiments since it does not alter the concentration of the two polyborane species. However, all other types of reaction can be discounted because, if any such reaction were to occur, the initial rate of consumption of B_5H_{11} would be at least doubled in the absence of H_2 because an extra mol of B_5H_{11} would be rapidly removed by the $\{B_4H_8\}$ produced in the initial slow step (3). Thus the conclusion from the hot/cold study[4] that the preferred route is *not* primarily *via* n-B_9H_{15} is reinforced by these detailed new kinetic results, and reaction (17) can therefore be eliminated

$$\{B_4H_8\} + B_5H_{11} \nrightarrow n\text{-}B_9H_{15} + 2H_2 \quad (17)$$

as an important step under the present conditions. Likewise, reaction (18) which Lipscomb[14] has suggested as an energetically favourable route to B_5H_9 in these interconversion

$$\{B_4H_8\} + B_5H_{11} \nrightarrow B_5H_9 + B_4H_{10} \quad (18)$$

reactions is also ruled out on this basis. As Lipscomb has remarked, if this reaction were to occur, the B_4H_{10} would be dissociated to $\{B_4H_8\}$ under the conditions of the experiment and the latter would behave as a catalyst for the production of H_2 from B_5H_{11}. In this case the addition of excess of H_2 to the reaction would be expected to have a dramatic effect on the initial rate of consumption of B_5H_{11}, which it manifestly does not.

One is therefore forced to conclude that the $\{B_4H_8\}$ produced in the initial step in the thermal decomposition of B_5H_{11} is consumed (in the absence of added H_2) not by reaction with a further mol of B_5H_{11} but with itself, just as the $\{BH_3\}$ which accompanies its production is presumed to react with itself to give B_2H_6. Long[15] has suggested that such an interaction might yield B_5H_9 plus the reactive intermediate $\{B_3H_7\}$, and in this way the formation of B_5H_9 in the thermolysis of B_5H_{11} alone is naturally accounted for, *i.e.* reaction (19). He also suggests that

$$2\{B_4H_8\} \longrightarrow B_5H_9 + \{B_3H_7\} \quad (19)$$

$$\{B_3H_7\} + \{B_4H_8\} \longrightarrow B_5H_9 + B_2H_6 \quad (20)$$

subsequent interaction between the two reactive intermediates might yield a further mol of B_5H_9 together with B_2H_6, as in reaction (20). However, from the overall initial stoicheiometry observed in our earlier study of B_5H_{11} alone it is clear that the interaction between two $\{B_4H_8\}$ molecules can, and must, proceed simultaneously through one or more other routes. The simplified picture discussed so far predicts a more rapid production of B_2H_6 and, in particular, B_5H_9 than is actually observed in the thermolysis of B_5H_{11} alone; moreover, the substantial production of polymer and H_2 in that reaction is not accounted for. It seems likely, therefore, that reactions such as those proposed by Shore and co-workers[8] in a different context, to account for the high-yield syntheses of B_4H_{10} and B_5H_{11} in solution at low temperature, may well be operative in these gas-phase systems also, *i.e.* reactions (9) and (15). Routes leading exclusively to polymer *via* reactive hexa- and octa-borane intermediates are also possible, *e.g.* reactions (8) and (21).[1] Such

$$2\{B_4H_8\} \longrightarrow \{\text{'}B_8H_{16-2n}\text{'}\}\text{(polymerizes)} + nH_2 \quad (21)$$

reactions involving the mutual interaction of, for example, two $\{B_4H_8\}$ molecules *via* different channels, *e.g.* reactions (19), (15), and (21), would undoubtedly be characterized by different Arrhenius parameters; *i.e.* their relative importance would depend on temperature. The fact that B_5H_{11} is produced essentially pure in the low-temperature synthesis, *via* the proposed[8] reaction (15), suggests that the latter has a very low activation energy (though it may also have a low frequency factor) compared with reaction (19), which apparently gains in importance somewhat at the higher temperatures employed in the gas-phase thermolysis of B_5H_{11}.[4]

Conclusions

In establishing that the activation energy ($E_a = 99.2 \pm 0.8$ kJ mol^{-1}) for the first-order thermal decomposition of B_4H_{10} remains unaltered in the presence of an excess of added H_2 ($E_a = 98.4 \pm 1.4$ kJ mol^{-1}), this work has provided compelling new evidence that the reversible unimolecular reaction (1) is the *sole* rate-determining step. The observed inhibition is then naturally explained in terms of the reverse reaction (−1), but the results raise doubts about the validity of subsequent steps in the previously proposed mechanism, and the need for further work is apparent.

In the case of B_5H_{11}, there is again a marked change in product distribution when an excess of H_2 is added to the system, but the initial rate remains unaltered by this addition over a wide range of temperature, and the activation energy is, therefore, unaltered also. The decomposition is thought to proceed *via* the rate-determining elimination of $\{BH_3\}$ [reaction (3)] followed by the rapid, and essentially 100% efficient, dimerization of the latter to give B_2H_6 [reaction (4)]. The $\{B_4H_8\}$ is scavenged by H_2 in the initial stages to give B_4H_{10} in high yield [reaction (−1)], but competitive reactions soon set in and the later stages of the B_5H_{11}/H_2 cothermolysis reflect many of the features displayed by the B_4H_{10}/H_2 system, most notably an increase in the production of B_2H_6 and a decrease in the formation of higher volatile boranes and involatile solids. A particularly interesting conclusion is that, in the absence of added H_2, $\{B_4H_8\}$ appears to react *not* with B_5H_{11} to give various products but with itself, *via* several alternative routes in temperature-dependent competition. Very low temperatures favour the regeneration of B_5H_{11} perhaps *via* reaction (15), whereas higher temperatures lead to B_5H_9 and involatile solids possibly *via* reactions such as (19) and (21).

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