A Kinetic Study of the Gas-phase Thermolysis of Pentaborane(11) *

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The kinetics of thermal decomposition of pentaborane(11) have been investigated by a mass-spectrometric technique in the pressure range 1.75—10.50 mmHg and temperature range 40—150 °C. In conditioned Pyrex vessels the reaction was shown to occur by a homogeneous gas-phase process according to the first-order initial-rate law $-d[B_5H_{11}]/dt = 1.3 \times 10^7 \exp(-72\,600/RT)[B_5H_{11}]$. The main volatile products are H_2 and B_2H_6, the latter appearing at the rate of *ca.* 0.5 mol per mol of B_5H_{11} consumed. Pentaborane(9) is also produced, at less than half the rate of B_2H_6, together with even smaller amounts of hexaboranes and $B_{10}H_{14}$, and traces of B_4H_{10}; some 40—45% of the boron is converted into involatile solid hydride BH_x, where x varies from *ca.* 2.0 at 40 °C to *ca.* 1.1 at 150 °C. No obvious dependence on temperature was detected in the overall distribution of boron between volatiles and solid, but the production of B_5H_9 was favoured at higher temperatures. Mechanistic implications of these results are discussed.

arachno-Pentaborane, B_5H_{11}, is the main volatile borane to be observed in the initial stages of the gas-phase thermolysis of B_2H_6 above about 100 °C. It is thought to be formed *via* *arachno*-B_4H_{10} as a result of the series of steps (1)—(6).[1] It must

$$B_2H_6 \rightleftharpoons 2\{BH_3\} \qquad (1)$$

$$\{BH_3\} + B_2H_6 \rightleftharpoons \{B_3H_9\} \qquad (2)$$

$$\{B_3H_9\} \rightleftharpoons \{B_3H_7\} + H_2 \qquad (3)$$

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

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

$$\{B_4H_8\} + B_2H_6 \longrightarrow B_5H_{11} + \{BH_3\} \qquad (6)$$

therefore play a major role in the ensuing sequence of complex interconversion reactions leading to *nido*-$B_{10}H_{14}$, but its precise contribution is not well understood.

Previous studies of the thermal decomposition of B_5H_{11} have been essentially qualitative in nature, and have not produced a consistent picture, even of the product analysis.[2–7] There has been no detailed study of the effect of varying the initial pressure and thermolysis temperature, and no attempt to establish the kinetics of the reaction. Indeed it was not entirely clear whether the decomposition is a homogeneous gas-phase process, or whether there is a heterogeneous component under certain conditions.[4]

As part of a systematic mass-spectrometric study of the kinetics of gas-phase thermolysis and cothermolysis reactions of the boranes,[8,9] we now report a detailed initial-rate study of the thermal decomposition of B_5H_{11} at pressures in the range 1.75—10.50 mmHg and temperatures of 40—150 °C. The work includes a series of careful experiments in packed vessels to establish the importance of any activity at the Pyrex surface, and to assess the effects of surface conditioning. Experiments involving the thermolysis of B_5H_{11} under hot/cold conditions are also reported. Some preliminary aspects of this work have been referred to elsewhere.[1]

Experimental

The stock of pentaborane(11) used in most of the kinetic studies was prepared from B_4H_{10} by the method of Shore and co-workers.[10] Early experiments were carried out with the same batch of material as that used in our recent electron-diffraction analysis.[11] It was purified by repeated fractionation on a low-temperature fractional distillation column, and was shown by ^{11}B n.m.r. spectroscopy to contain <0.5% B_5H_9 as the only detectable impurity; its vapour pressure at 0 °C was 52.5 mmHg, in excellent agreement with the published value.[2] The sample used in the 'packed-vessel' study (see later) was prepared from B_5H_9 by the more recent method of Wermer and Shore[12] using potassium dihydronaphthylide as the reducing agent. Standard grease-free vacuum-line techniques were used throughout.

The quantitative mass-spectrometric techniques involving continuous capillary sampling of the heated reaction mixture have been described previously together with details of the methods of data analysis.[8,9] All thermolyses were carried out in 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, made up to our specifications by BOC Ltd. As indicated in the Results section, the bulbs were either unpacked (volume *ca.* 1.1 dm^3), or packed with Pyrex Raschig rings to give a 33-fold increase in surface-to-volume ratio (volume *ca.* 0.79 dm^3). The bulbs (and any packing) were first washed with water, acetone, and light petroleum, and then baked out under vacuum at *ca.* 150 °C; except where otherwise indicated, they were conditioned prior to use as already discussed.[9]

Hot/cold thermolyses were carried out in a concentric-tube reactor with an annular volume of 1.2 dm^3, similar to that described by Klein *et al.*[13] The outer surface was cooled to 0 °C whilst the inner surface was heated to temperatures in the range 110—205 °C by means of a coil immersed in silicone fluid (Dow Corning 550). Typical initial pressures of B_5H_{11} were 21 and 40 mmHg.

Results

General Features.—Typical reaction profiles for the thermolysis of B_5H_{11} at 110.4 and 150.7 °C are shown in Figures 1 and 2, respectively, for an initial pressure of *ca.* 3.5 mmHg; a complete set of reaction profiles for the thermolyses discussed in this work can be found elsewhere.[14] From these results it is clear

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

Table 1. Initial-rate data for thermolysis of B_5H_{11}

T/K	$p_0(B_5H_{11})$/mmHg	$10[B_5H_{11}]_0$/mol m^{-3}	$-10^6(d[B_5H_{11}]/dt)_0$	$10^6(d[H_2]/dt)_0$	$10^6(d[B_2H_6]/dt)_0$
				mol m^{-3} s^{-1}	
313.4	3.53	1.81	2.4	0.6	1.1
322.7	3.49	1.73	3.6	1.5	1.5
333.6	3.50	1.68	7.3	3.7	6.5
349.1	1.75	0.80	13.9	6.4	10.4
348.5	3.02	1.39	17.9	12.4	14.8
347.9	3.47	1.60	30.2	11.5	*
348.2	5.29	2.44	43.5	27.1	25.1
347.5	6.88	3.17	56.4	30.4	41.8
347.8	10.36	4.78	79.4	34.8	59.2
363.9	3.53	1.56	76.3	32.8	*
373.0	3.52	1.51	198	55.2	57.3
383.5	3.47	1.45	264	184	170
398.4	3.52	1.42	667	418	626
423.8	3.50	1.32	1 548	1 194	1 135

* Unreliable data because of incorrect level settings.

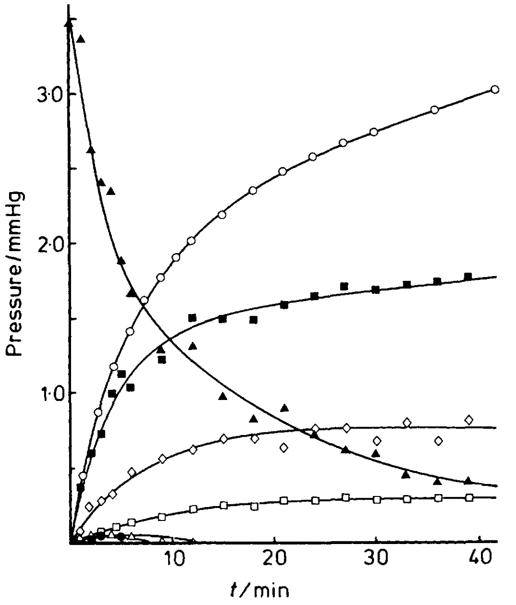

Figure 1. Reaction profile for the thermolysis of B_5H_{11} (p_0 = 3.47 mmHg) at 110.4 °C: (○) H_2, (▲) B_5H_{11}, (■) B_2H_6, (◇) B_5H_9, (□) $B_{10}H_{14}$, (●) B_4H_{10}, and (△) B_6H_{12}

that the thermolysis is an exceedingly complex reaction; several volatile products appear from the moment the gaseous mixture enters the heated reaction vessel, and (see later) there is a concurrent deposition, predominantly on the lower surfaces of the reaction vessel, of a pale yellow involatile solid hydride.

The main volatile products, in decreasing order of amount on a molar basis, are hydrogen, B_2H_6, B_5H_9, and $B_{10}H_{14}$; smaller amounts of B_4H_{10} and B_6H_{12}, and traces of B_8H_{12} and B_9H_{15} are also observed. There is, however, some temperature dependence in the product distribution: B_5H_9 is produced in slightly greater quantities in runs carried out at the higher temperatures, whereas B_4H_{10} is more abundant at lower temperatures (below 100 °C). There is also some indication that formation of B_2H_6 is favoured by lower temperatures and $B_{10}H_{14}$ by higher temperatures, but the differences are small compared with the associated errors and may not be significant. The rate of formation of H_2 relative to the rate of consumption of B_5H_{11} appears to increase as the temperature is raised. These results are presented in a more quantitative form in later sections.

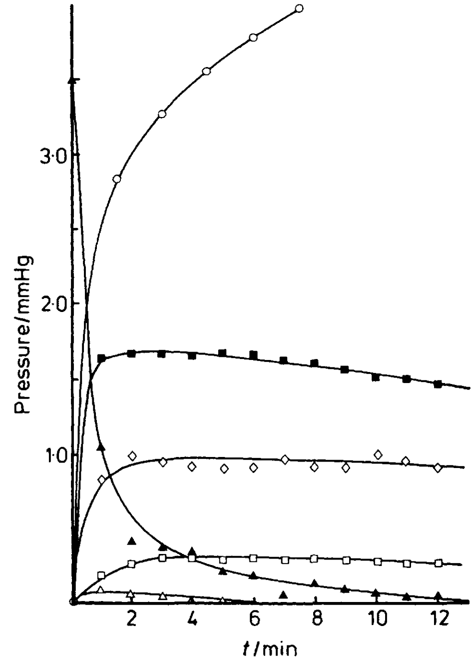

Figure 2. Reaction profile for the thermolysis of B_5H_{11} (p_0 = 3.50 mmHg) at 150.7 °C: symbols as in Figure 1

The reaction at 150.7 °C (Figure 2) is very rapid indeed, being virtually complete within about 3—4 min. Thereafter, the concentrations of the main volatile borane products (B_2H_6 and B_5H_9) remain essentially constant, indicating that there is little reaction between them, despite the relatively high temperature. In this respect it is interesting that $B_{10}H_{14}$ is formed only during the early part of the thermolysis, and no longer continues to build up after the B_5H_{11} has been consumed.

Kinetic Studies.—In common with other borane thermolyses, the decomposition of B_5H_{11} rapidly produces a complex mixture, and for this reason we have studied the kinetics by the initial-rate method to minimize the effects of interference from products.

Reaction order. Initial rates of consumption of B_5H_{11} and production of H_2 and B_2H_6 were measured at 75.1 ± 0.5 °C for six pressures in the range 1.75—10.36 mmHg. The initial rates were obtained by the tangent method from reaction profiles of

Table 2. First-order rate constants for thermolysis of B_5H_{11} [a]

T/K (±0.5)	$10^6k_{1,B_5H_{11}}$	$10^6k_{1,H_2}$	$10^6k_{1,B_2H_6}$
		s^{-1}	
313.4	13.1	3.4	5.9
322.7	20.7	8.4	8.8
333.6	43.4	22.2	38.3
348.2	168 ± 19 [b]	86.8 ± 13.8 [b]	118 ± 12 [b]
363.9	491	211	
373.0 [c]	1 310	365	379
383.5	1 820	1 260	1 170
398.4	4 710	2 950	4 420
423.8	11 700	9 010	8 570

[a] The data listed are evaluated from the expressions $k_{1,B_5H_{11}} = -(d[B_5H_{11}]/dt)_0/[B_5H_{11}]_0$, $k_{1,H_2} = (d[H_2]/dt)_0/[B_5H_{11}]_0$, and $k_{1,B_2H_6} = (d[B_2H_6]/dt)_0/[B_5H_{11}]_0$. Errors are estimated to be *ca.* 5—10%. [b] Mean values taken from six runs at this temperature (see Table 1); errors quoted are standard deviations. [c] From Figure 4 it is apparent that the ln k_1 values for both consumption of B_5H_{11} and production of H_2 fall off the lines of least-squares best fit; moreover, the deviations occur in opposite senses, thereby maximizing any errors in the value of the ratio $k_{1,H_2}/k_{1,B_5H_{11}}$ (see text), and in the results of mass-balance calculations based on these data (see Table 3, footnote *a*).

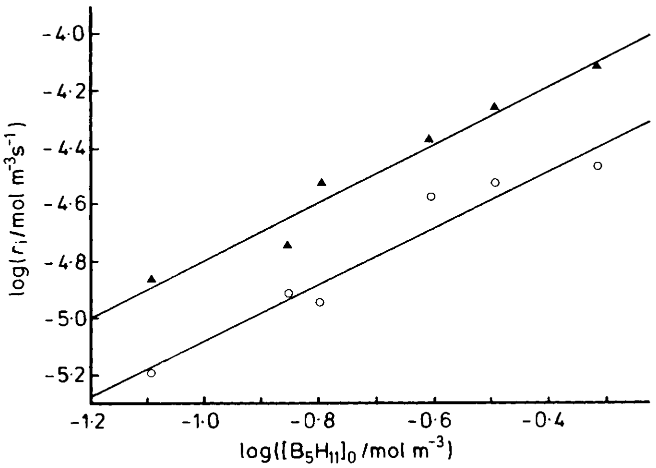

Figure 3. Logarithm of the initial rate (r_i) *versus* the log of the initial concentration of B_5H_{11} for thermolyses at 75.1 °C. Filled triangles refer to B_5H_{11} consumption and open circles to hydrogen production. The slopes of the lines of least-squares best fit to the two sets of data (*i.e.* the reaction orders with respect to $[B_5H_{11}]$) are, respectively, 1.04 ± 0.11 and 1.02 ± 0.13. A similar plot for the production of B_2H_6 yields a slope of 1.01 ± 0.09. Correlation coefficients lie between 0.97 and 0.99

Table 3. Stoicheiometry of the involatile solid as a function of temperature [a]

T/K	t^b/min	Stoicheiometry, x in BH_x
313.4	84	2.0
322.7	44	1.9
333.6	28	1.6
348.2	15	1.6
383.5	6	1.2
398.4	2	1.2
423.8	2	1.1

[a] A value of x = 1.9 determined at 373.0 K is probably erroneous and is omitted from the Table (see Table 2, footnote *c*). [b] Reaction time at which calculation was carried out.

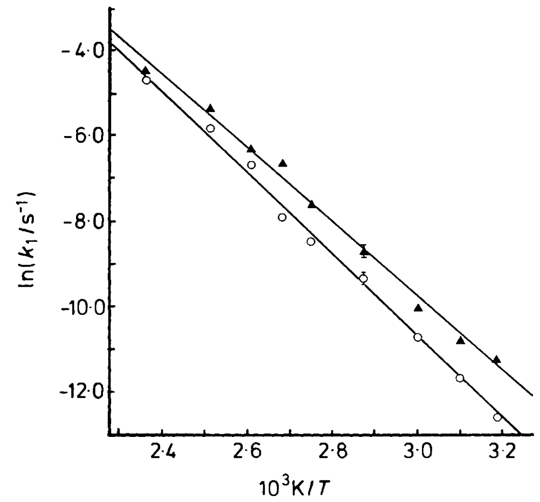

Figure 4. Arrhenius plots based on initial-rate constants for the consumption of B_5H_{11} (▲) and appearance of H_2 (○) in the thermal decomposition of B_5H_{11}. The data points at 75 °C are mean values from six separate runs; standard deviations are indicated by error bars

the type shown in Figures 1 and 2. The results are included in Table 1 and recorded in the form of log–log plots in Figure 3. The slopes of the lines of least-squares best fit to the data are very close to unity in all cases (see caption to Figure 3), indicating that the reaction is accurately first order.

Activation energy. The activation energy of the thermal decomposition of B_5H_{11} was determined by recording the first-order rate constants at nine temperatures in the range 40—150 °C. Initial rates are given in Table 1, together with the data already discussed, and the rate constants are recorded in Table 2. Arrhenius plots of the data are shown in Figure 4 for the consumption of B_5H_{11} and production of hydrogen. Excellent linear plots were obtained not only for these but also for the production of B_2H_6 (not shown, see ref. 14). The values of the activation energies obtained from the slopes of these plots are $E_{a,B_5H_{11}}$ = 72.6 ± 2.4, E_a (from H_2 production) = 80.1 ± 2.0, and E_a (from B_2H_6 production) = 76.3 ± 3.5 kJ mol^{-1}; the corresponding pre-exponential factors obtained from the intercepts are $A_{B_5H_{11}} = e^{16.4 \pm 0.8}$ (*ca.* 1.3 × 10^7), A (from H_2 production) = $e^{18.2 \pm 0.7}$ (*ca.* 7.8 × 10^7), and A (from B_2H_6 production) = $e^{17.1 \pm 1.2}$ (*ca.* 2.7 × 10^7) s^{-1}.

Reaction Stoicheiometry, and Composition of the Involatile Solid.—As discussed earlier, the thermolysis of B_5H_{11} is a complex reaction in which several products are formed simultaneously from the moment the mixture is heated. Hydrogen and B_2H_6 are formed in relatively large amounts, and their initial rates of appearance can therefore be measured with reasonable precision and accuracy; the same is true of the initial rate of consumption of the B_5H_{11} itself (see Table 1). It is generally a much more difficult problem to obtain reliable and reproducible initial-rate data for the minor products, and for this reason we have not attempted to specify an overall *initial* stoicheiometry for the reaction. The initial-rate data in Table 2 indicate that, on average, 1 mol of B_5H_{11} *initially* generates 0.6 ± 0.2 mol of B_2H_6 and 0.5 ± 0.2 mol of H_2, though it is important to note that this latter average value conceals a marked temperature dependence. The relative rates of production of H_2 and B_2H_6 are, in fact, *time*-dependent as is clear from Figures 1 and 2. The implications of these observations become apparent when mass-balance calculations are carried out to

Table 4. Initial-rate data (mol m^{-3} s^{-1}) for the thermolysis of B_5H_{11} (p_0 = 3.50 mmHg[a]) in a packed vessel at 74 °C[b]

Run no.[c]	$-10^6(d[B_5H_{11}]/dt)_0$	$10^6(d[H_2]/dt)_0$	$10^6(d[B_2H_6]/dt)_0$	$10^6(d[B_5H_9]/dt)_0$
1	218	16	118	29
2	64	8	27	10
3	34	9	15	
4	31	10	18	8
5	30	10	16	9
6	30	12	14	10

[a] 0.162 mol m^{-3}. [b] Average temperature over six runs 347.0 ± 0.4 K. [c] Runs 1—6 correspond to consecutive thermolyses in an initially clean vessel, packed with Raschig rings to give a 33-fold increase in the ratio surface area/volume.

determine the approximate amount and composition of the involatile solid hydride formed in these thermolyses. In fact, some 40—45 atom% of the boron content of the reacted B_5H_{11} appears as an involatile solid and this proportion is essentially independent of temperature. In contrast (see Table 3), the hydrogen content of the solid is markedly dependent on temperature, its composition varying from $BH_{2.0}$ at 40 °C to $BH_{1.1}$ at 150 °C.

Surface Studies.—To check for possible surface activity, six consecutive thermolyses were carried out at 74 °C in an initially clean Pyrex vessel packed with Raschig rings as described in the Experimental section. The initial pressure of B_5H_{11} in each case was 3.5 mmHg. From the results in Table 4 it can be seen that the initial rate of decomposition of B_5H_{11} in the first run is almost an order of magnitude greater than that observed (see Table 1) for the run at the same temperature and initial pressure in an unpacked, conditioned vessel (2.18×10^{-4} compared with 0.3×10^{-4} mol m^{-3} s^{-1}). However, in successive runs the initial rate slows down and eventually stabilizes at the same value as that observed for the thermolysis in an unpacked (conditioned) vessel. The initial rates of production of H_2, B_2H_6, and B_5H_9 in the *conditioned*, packed vessel are also similar to those in the unpacked vessel. The mechanistic significance of this important result is discussed later.

It is also clear from Table 4 that the initial rate of production of B_2H_6 ($r_{i.B_2H_6}$) relative to the initial rate of consumption of B_5H_{11} ($r_{i.B_5H_{11}}$) is about the same in all the packed-vessel runs, regardless of the extent of conditioning. For the six experiments the average value observed for the ratio $r_{i.B_2H_6}/r_{i.B_5H_{11}}$ is 0.51 ± 0.06, which is in excellent agreement with the value of 0.52 derived from the least-squares best fits to the data recorded at this temperature (74 °C) for the thermolysis in an unpacked vessel and with the average value of 0.6 ± 0.2 for all measurements referred to earlier. In contrast, there is a dramatic increase in the relative product of H_2 as the packed vessel becomes conditioned. Thus, in successive runs the ratio $r_{i.H_2}/r_{i.B_5H_{11}}$ increases steadily from 0.07 to 0.40, the final value being again in good agreement with the value of 0.44 taken from the data in Figure 4 for runs in a conditioned, unpacked vessel. There may be a similar trend in the initial rate of production of B_5H_9 but in view of the large errors involved in determining the initial rate of formation of this minor product, these values should be treated with caution. The average value of 0.24 ± 0.08 for the ratio $r_{i.B_5H_9}/r_{i.B_5H_{11}}$ is probably a more meaningful quantity, and this implies that the B_5H_9 is produced at slightly less than half the rate of B_2H_6 at this temperature.

Discussion

The thermal decomposition of B_5H_{11} has been studied qualitatively by several groups in the past, with differing results, but no detailed kinetic work on the system has been published. Burg and Schlesinger,[2] Bragg *et al.*,[3] and Morrey and Hill[4] have all identified H_2 and B_2H_6 as the major volatile products, but have given no specific indication of their rates of formation relative to the rate of consumption of B_5H_{11}. The compound B_5H_9 has been detected as a stable product in all of these studies, but opinions have differed as to whether it is formed from the very beginning of the thermolysis[3,4,7] or at a later stage when many other species are present.[2] Similar doubts have existed concerning the time at which the involatile solids appear, and B_4H_{10}, B_8H_{12}, and $B_{10}H_{14}$ have been detected in some studies but not in others. The present study has shown that these species are indeed all formed, together with minor amounts of B_6H_{12} and traces of B_9H_{15}. It is also clear that B_5H_9 and involatile solids are produced from the beginning of the reaction. In the case of B_5H_9 we were ourselves mistaken on this point in the early stages of our work, after analysing several runs at the lower end of the temperature range, where there are difficulties in detecting B_5H_9 because of its relatively slow rate of formation.[1]

The initial step in the thermolysis of B_5H_{11} is now generally thought to be the dissociation (7), and the important

$$B_5H_{11} \longrightarrow \{B_4H_8\} + \{BH_3\} \qquad (7)$$

observation from molecular-beam studies[6] that $\{B_4H_8\}$ and $\{BH_3\}$ are present in the thermolysis of B_5H_{11} in a flow reactor adds weight to this. Moreover, the present work, in establishing that the reaction follows first-order kinetics, and that B_2H_6 is produced at the rate of *ca.* 0.5 mol per mol of B_5H_{11} consumed, leaves little room for doubt that (7) is indeed the rate-determining step. The observed rate of production of B_2H_6 is then readily explained by its formation from the rapid combination of two $\{BH_3\}$ units *via* the reverse of equation (1) with *ca.* 100% efficiency. In agreement with previous speculation,[15,16] the direct unimolecular liberation of H_2 from B_5H_{11} to give B_5H_9 can therefore be eliminated as an important initial step in this reaction. To account for the formation of B_5H_9, Schaeffer[16] has proposed the unlikely sequence of events in which two hydrogen atoms are transferred from B_5H_{11} to B_4H_{10}, which then splits up to give two molecules of B_2H_6. This reaction seems never to have been put to the test, either in a separate cothermolysis reaction or in an isotopic labelling experiment, but for reasons which have been put forward by Long[15] it must be considered very doubtful. A most unsatisfactory feature of this proposed reaction is that it relies on the prior production of B_4H_{10}, *via* the (assumed) rate-controlling interaction of B_5H_{11} with H_2 formed from minor secondary reactions or by hydrolysis resulting from the presence of traces of water on the walls. On the basis of the present results this hypothetical sequence is no longer tenable.

Another possibility is that the B_5H_9 results from the interaction of B_5H_{11} with the $\{B_4H_8\}$ production in equation (7). Lipscomb[17] has calculated that this reaction (8), which also

$$\{B_4H_8\} + B_5H_{11} \longrightarrow B_4H_{10} + B_5H_9 \qquad (8)$$

produces B_4H_{10}, is exothermic by 125.5 kJ mol^{-1}. As Lipscomb has pointed out, at the temperatures required to decompose B_5H_{11}, B_4H_{10} would be appreciably dissociated to $\{B_4H_8\}$ and H_2, so that $\{B_4H_8\}$ would be essentially a catalyst for the loss of H_2 from B_5H_{11} in this reaction. Although this step cannot be entirely ruled out on the basis of the present results, it is clear from the relatively slow rate of production of B_5H_9 that it is certainly not the main route by which the $\{B_4H_8\}$ is consumed. An alternative possibility is that $\{B_4H_8\}$ reacts with B_5H_{11} to produce hydrogen and B_9H_{15}, followed rapidly by the decomposition of the latter to give 'polymer' and $B_{10}H_{14}$.[15] However, in the present work, thermolysis of B_5H_{11} under hot/cold conditions, produced negligible amounts of B_9H_{15}, and $B_{10}H_{14}$ (which is a likely stable product from n-B_9H_{15} under thermolytic conditions) did not build up in quantity, either in the hot/cold experiments or in the normal thermolysis reactions.

It has been suggested that $\{B_4H_8\}$ can react with *itself* to produce $\{B_3H_7\}$ and B_5H_9, and subsequently with the $\{B_3H_7\}$ to produce B_2H_6 and more B_5H_9 [reactions (9) and (10)

$$\{B_4H_8\} + \{B_4H_8\} \longrightarrow B_5H_9 + \{B_3H_7\} \qquad (9)$$

$$\{B_3H_7\} + \{B_4H_8\} \longrightarrow B_5H_9 + B_2H_6 \qquad (10)$$

respectively].[15] these reactions may well be operative, but it is clear that other processes are also occurring, because insufficient B_5H_9 is produced initially, and a significant proportion of the $\{B_4H_8\}$ appears to be converted into non-volatile BH_x solid. Even if all the $\{B_3H_7\}$ produced in (9) were diverted to give 'polymer,' it would still be necessary to invoke other reaction channels involving the production of 'polymer' from $\{B_4H_8\}$. Possibilities could include reactions (11) and (12).

$$\{B_4H_8\} + \{B_4H_8\} \longrightarrow \text{solid 'polymer'} + mH_2 \qquad (11)$$

$$\{B_4H_8\} + \{B_4H_8\} \longrightarrow B_5H_{11} + \text{solid 'polymer'} + nH_2 \qquad (12)$$

The latter was invoked by Shore and co-workers[10] to explain the high-yield synthesis of B_5H_{11} in the low-temperature reactions involving hydride-ion abstraction from $[B_4H_9]^-$. In view of the observed temperature dependence in the yield of B_5H_9 in the thermolysis of B_5H_{11}, it is possible that reactions such as (9) and (12) are in a temperature-dependent competition, with the former being favoured at higher temperatures. Details of the amount of H_2 produced in these thermolyses and its temperature dependence can also be understood in terms of steps such as these.

Of the other boranes formed in this system, B_4H_{10} has only a fleeting existence because of its thermal instability at the temperatures employed.[9] It is undoubtedly formed from the reaction between $\{B_4H_8\}$ and H_2 generated in the reaction. Hexaboranes appear in the form of B_6H_{12}, but the concentrations are very small and the mechanism of formation is uncertain. The compound $B_{10}H_{14}$ *does* become an important final product, and it is interesting that it no longer continues to build up rapidly when the B_5H_{11} has been consumed. This is illustrated in Figure 2, which shows the reaction profile at 150 °C. The observation that the concentrations of B_2H_6, B_5H_9, and $B_{10}H_{14}$ become more or less constant could be taken to indicate that the latter is not formed in this system from the cothermolysis of the two smaller boranes. However, this is probably an erroneous conclusion, and it is likely that the lack of reaction in the later stages of the thermolysis can be attributed to the inhibiting effect of the substantial amount of H_2 that has accumulated. The route to $B_{10}H_{14}$ in the B_2H_6/B_5H_9 cothermolysis system is thought to proceed *via* the interaction of $\{B_3H_7\}$ [formed in steps (1)—(3)] with B_5H_9.[15] In the later stages of the B_5H_{11} thermolysis there will be a competition between H_2 and B_5H_9 for the $\{B_3H_7\}$, and it seems likely that H_2 is successful in reversing the sequence (1)—(3), thereby reducing the amount of $\{B_3H_7\}$ available for reaction with B_5H_9.

The results of the packed-vessel study are of crucial importance in establishing that the thermolysis of B_5H_{11} in 'conditioned' vessels is a homogeneous gas-phase reaction. In consequence, the activation parameters, which have been determined for the first time in this work, can be meaningfully compared with those recorded for gas-phase decompositions of other boranes. Thus, the activation energy of B_5H_{11} (72.6 ± 2.4 kJ mol^{-1}) is considerably less than that for B_4H_{10} (99.4 ± 3.4 kJ mol^{-1}), reflecting a more dramatic temperature dependence of the rate constant for the latter. More specifically, the ratio of the first-order rate constants ($k_{1,B_4H_{10}}/k_{1,B_5H_{11}}$) is found to vary from 49 at 200 °C to 1.7 at 40 °C, implying that the two boranes should have similar stabilities at the lower temperatures. At first sight it may therefore seem surprising that, in the thermolysis of B_4H_{10},[9] B_5H_{11} builds up to the extent that it does. It must be remembered, however, that both $\{B_4H_8\}$ and $\{BH_3\}$ (which are the initial products of the decomposition of B_5H_{11}) may themselves react further with B_4H_{10} to regenerate B_5H_{11}. Nevertheless, these considerations highlight the need for caution in interpreting the initial-rate data in terms of possible stoicheiometries in such complex interconversion systems.

The value of 1.6×10^7 s^{-1} for the pre-exponential factor for the thermolysis of B_5H_{11} is lower by four orders of magnitude than the value for B_4H_{10} (6×10^{11} s^{-1}), consistent with the gross differences proposed for the initial steps in the two decompositions, *viz*. elimination of BH_3 and of H_2, respectively. The value for B_4H_{10} itself is at the lower end of the range of values (*ca*. 10^{11}—10^{15} s^{-1}) found for unimolecular decompositions of hydrocarbon derivatives,[18,19] and is acceptable for a mechanism involving release of H_2 *via* a loosely bound transition state. The pre-exponential factor for the decomposition of B_5H_{11} as determined both from the rate of consumption of the reactant and from the appearance of the products (*e.g.* H_2 or B_2H_6) is exceptionally low, and at first sight might appear to cast doubt on the validity of the proposed mechanism involving (7) as the initial, unimolecular, rate-determining step. However, we believe that there are cogent reasons for accepting this unusual value. First, a very similar A value (and E_a value) has recently been observed in the gas-phase decomposition of B_6H_{12},[20] whose structure[21] is closely related to that of B_5H_{11}. Secondly, it is important to appreciate that these are among the first reliable experimental data on Arrhenius parameters to be reported for the boron hydrides, which are in fact a particularly unusual class of compounds whose unique structural and bonding properties could well engender unexpected kinetic parameters. The much lower A factor for B_5H_{11} compared with B_4H_{10} may reflect considerable reorganization in a tightly bound transition state, consistent with the more extensive changes that would accompany the release of a BH_3 group from the cluster. An additional point is that the slow initial step (7) is expected to dominate the overall Arrhenius parameters for the reaction and, though subsequent rapid steps such as (8) and (12) which consume or regenerate B_5H_{11} will of course contribute, it is most unlikely that these would lead to a reduction of several orders of magnitude in the observed pre-exponential factors.

The dramatic increase in the rate of decomposition of B_5H_{11} in a clean, packed vessel is reproducible and implies that the reaction is catalysed by the clean Pyrex surface. Evidence that this is the case, and that a spurious reaction with adsorbed moisture or other species is not occurring, comes from the observation that the rate of production of B_2H_6 relative to the rate of consumption of B_5H_{11} remains the same, regardless of the extent or condition of the surface. The rate-controlling initial step is therefore the same [*i.e.* reaction (7)] as in the homogeneous gas-phase reaction, but is accelerated. The data are not sufficiently accurate to reveal any major changes in product distribution, apart from the dramatic reduction in the relative production of H_2 in the clean, packed vessel. It seems most unlikely that this is caused by adsorption of H_2 on the surface, and implies that the formation of a hydrogen-rich solid is favoured under these conditions. It should perhaps be noted that Morrey and Hill[4] have suggested that B_5H_{11} may be converted catalytically into B_5H_9 by the presence of a brass surface, but this does not occur at the Pyrex surface in our experiments.

Conclusions

In the temperature range 40—150 °C and pressure range 1.75—10.5 mmHg the homogeneous gas-phase decomposition of B_5H_{11} has been shown to proceed with first-order kinetics and an activation energy of 72.6 ± 2.4 kJ mol^{-1}. The initial step [equation (7)] involves the release of a BH_3 group from B_5H_{11} *via* a tightly bound transition state, and this is followed by the rapid dimerization of $\{BH_3\}$ to give B_2H_6 with *ca.* 100% efficiency. The precise fate of the fugitive $\{B_4H_8\}$ intermediate is more complex in this reaction system and the relative importance of various possible routes has not been established in detail; it may react with itself *via* several channels [*e.g.* reactions (9), (11), and (12)] in temperature-dependent competition, or with B_5H_{11} [reaction (8)], to give the final products which are mainly B_5H_9 and involatile solids, though $B_{10}H_{14}$ also accumulates.

The effect of added hydrogen on the thermolysis of B_5H_{11} has been studied in detail in an attempt to resolve these and related mechanistic questions. The results of these further studies and those of added hydrogen on B_4H_{10} are the subject of a subsequent paper.

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