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

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The kinetics of thermal decomposition of tetraborane(10) have been investigated by a mass spectrometric technique in the pressure range 0.86—38.69 mmHg and temperature range 40.3—77.9 °C (313.4—351.0 K). The initial rate of consumption of B_4H_{10} follows the first-order rate equation $-d[B_4H_{10}]/dt = 6.4 \times 10^{11} \exp(-99\,400/RT)[B_4H_{10}]$, with no evidence for the $\frac{3}{2}$-order dependence claimed in the most recent literature. In the *initial* homogeneous gas-phase reaction, B_5H_{11} is produced with an order slightly greater than unity, and at a rate of 0.4—0.5 mole per mole of B_4H_{10} consumed; hydrogen is also produced, with first-order kinetics, together with non-volatile solid hydride. Significant induction periods are observed in the build-up of species other than B_5H_{11} (*i.e.* B_2H_6, B_6H_{12}, and $B_{10}H_{14}$), indicating that they are the result of reactions subsequent to those involved in the initial stages. The initial reaction is interpreted in terms of the three-step mechanism, (1a), (2), and (3), in which (1a) is rate-limiting. A possible fourth step (5) may be an additional minor reaction favoured at low pressures.

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

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

$$\{B_3H_7\} + \{B_3H_7\} \longrightarrow \{\text{'}B_6H_{14-2m}\text{'}\}\ (\text{polymerizes}) + mH_2 \qquad (3)$$

$$\{B_4H_8\} + \{B_4H_8\} \longrightarrow \{\text{'}B_8H_{16-2n}\text{'}\}\ (\text{polymerizes}) + nH_2 \qquad (5)$$

There is a disconcerting lack of agreement in the published literature dealing with the kinetics of thermolysis of tetraborane(10).[1–6] We have summarized much of the background to this recently,[7] and it is sufficient to recall that uncertainty exists over such crucial kinetic and mechanistic aspects as the order of the reaction, the magnitudes of the observed rate constants, the activation energy, and in particular the nature of the initial step.

In an attempt to clarify the situation we have investigated the kinetics of the *initial* reaction in detail at four temperatures in the range 40.3—77.9 °C (313.4—351.0 K), using a recently developed method of quantitative mass spectrometry which allows all volatile components of the mixture (including hydrogen) to be monitored continuously. The results resolve many of the earlier inconsistencies and give important new insights into the mechanism.

Experimental

Tetraborane(10) was prepared, purified, and handled by methods referred to elsewhere.[7] It was thermolysed in a spherical Pyrex bulb (volume *ca.* 1 dm^3) in the presence of an excess of helium gas (partial pressure 100 mmHg). Argon (5 mmHg) and krypton (3.75 mmHg) were also included for calibration purposes. As indicated in the Results section, the bulb was either unpacked, or packed with glass Raschig rings (6 mm long, 6 mm external diameter, 1 mm wall thickness) so as to give a 33-fold increase in the surface area: volume ratio. Except where otherwise indicated, the bulb was conditioned by prior exposure to a heated borane mixture. The progress of each reaction was followed by two mass spectrometers: a Kratos MS30 instrument coupled to a DS55 data system to monitor the boranes, and an MS10S to analyse for dihydrogen. The MS30 ion source was conditioned prior to each set of measurements by allowing a sample, identical in composition to that used in the actual thermolysis, to bleed into the mass spectrometer until the response became stable. Other details of the instrumentation and procedures have already been reported.[8]

It should be stressed that it is by no means straightforward to obtain accurate quantitative kinetic data by mass-spectrometric analysis of borane mixtures. In principle, our methods provide a means of obtaining an instantaneous analysis of all gaseous components of a reacting mixture, without disturbing the bulk of the sample. In practice, it is necessary to exercise extreme care to ensure that the results are quantitatively meaningful. There are two main areas of difficulty. First, it is necessary to give careful thought to the conditions under which the sample flows from the reaction vessel into the mass spectrometer.[8] Secondly, it is important that the mass spectrometer should respond reproducibly and self-consistently to individual components of the mixture. Mass discrimination is potentially a major problem in the analysis of boranes, because of the adverse effect which these materials have on the ion source. The effects are, however, minimised by the source-conditioning techniques referred to earlier and it is possible to apply correction factors to take account of small residual discrepancies as already outlined.[8] In monitoring the disappearance of a reactant (*i.e.* B_4H_{10} in the present context) the required factors can be determined accurately, and provided the effects of mass discrimination remain constant during the run, the problem is adequately dealt with. We now use krypton as an additional marker along with argon to indicate the extent of any non-uniform changes in response across the mass range during a run, thereby providing a criterion for rejecting potentially unreliable data. In the analysis of a *product*, it is difficult to establish experimentally the precise factor required to correct the data, and the errors are

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

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

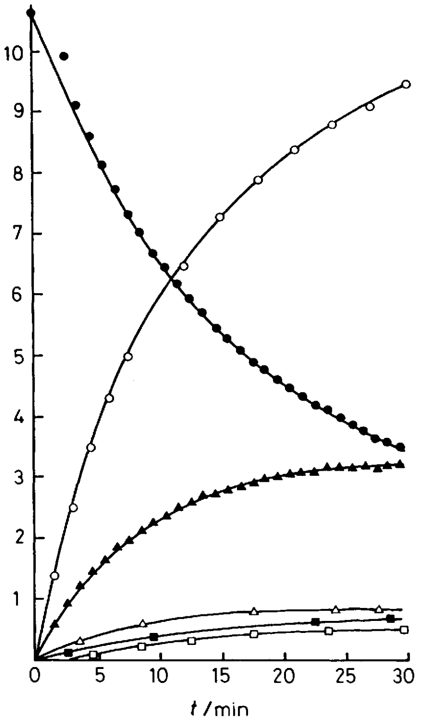

Figure 1. Reaction profile for the thermolysis of B_4H_{10} (p_0 = 10.65 mmHg) at T = 351 K: (○) H_2, (●) B_4H_{10}, (▲) B_5H_{11}. For clarity, only selected data points have been plotted for the minor species (■) B_2H_6, (△) B_6H_{12}, and (□) $B_{10}H_{14}$

therefore likely to be somewhat greater than those associated with the analysis of a species present at the outset. Fortunately, these effects tend to be random and, by comparing results obtained on different occasions and with different ion sources, it is generally possible to arrive at a consistent product analysis. The hydrogen measurements are virtually free from the effects of mass discrimination, principally because the boranes, which would otherwise give rise to source conditioning effects, are removed[8] from the gas stream before it enters the MS10S. As a result, the hydrogen data are intrinsically more accurate than the borane data.

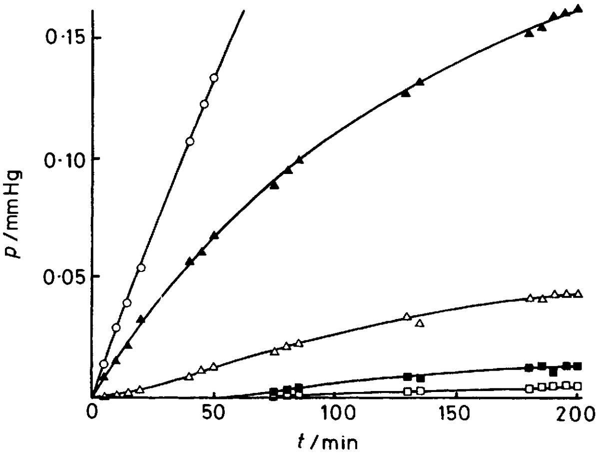

Figure 2. Reaction profile at high spectrometer gain showing the build-up of the volatile boranes during the initial stages of a thermolysis of B_4H_{10} (p_0 = 3.89 mmHg) at T = 313.4 K: (○) H_2, (▲) B_5H_{11}, (△) B_6H_{12}, (□) $B_{10}H_{14}$, (■) B_2H_6. For clarity, data points for B_2H_6 and $B_{10}H_{14}$ have been omitted from the diagram in the early stages of the reaction, where their concentration was zero

Table 1. High-resolution measurements on hexaborane observed in the thermal decomposition of B_4H_{10}*

Fragment	m/z (obs.)	m/z (calc.)	Relative intensity
$^{11}B_6H_{10}$	76.1348	76.1341	100 ± 4
$^{10}B_1{}^{11}B_5H_{11}$	76.1459	76.1455	30 ± 4
$^{10}B_2{}^{11}B_4H_{12}$	76.1569	76.1570	4 ± 4
$^{11}B_6H_{11}$	77.1422	77.1419	weak
$^{10}B_1{}^{11}B_5H_{12}$	77.1546	77.1534	weak

* A sample of B_4H_{10} (p = 18 mmHg in *ca.* 1 dm^3) was heated at 75 °C for *ca.* 16 min. The mixture was fractionated at −63 °C to remove B_2H_6, unreacted B_4H_{10}, and a significant proportion of the B_5H_{11} present. The hexaborane fraction was then examined under high resolution (11 000).

Results

Reaction Profile.—A typical reaction profile for the thermolysis of B_4H_{10} at 351 K is shown in Figure 1 for an initial pressure of 10.65 mmHg. The main volatile products (hydrogen and B_5H_{11}) are accompanied by smaller amounts of B_2H_6, B_6H_{12}, and $B_{10}H_{14}$, but there is no evidence for the formation of significant amounts of either B_5H_9 or B_6H_{10} in the early stages of the reaction. The mass spectra of mixtures of B_5H_9 and B_5H_{11} can readily be deconvoluted to reveal the relative contributions to the total ion current from the individual components, because the profiles of the two boranes differ significantly. This is not the case for B_6H_{10} and B_6H_{12} and, to throw further light on the problem, the hexaborane species from a fractionated reaction mixture were examined under high resolution to separate the various isotopomers. The presence of three resolved peaks at m/z 76 (Table 1), along with two peaks at m/z 77, confirms the presence of B_6H_{12}, and from their relative intensities it is apparent that there is little evidence for admixture of B_6H_{10}. Earlier work[9] gave intensity ratios of 100:45:11 for the three peaks at m/z 76, compared with our observed ratios of 100:30:4. However, the earlier study employed a slightly lower source temperature than that used in the present work (*ca.* 70 °C compared with *ca.* 85 °C) and this could account for the slight discrepancy. The distribution of boron between the various volatile products is largely independent of temperature and initial pressure of B_4H_{10}.

In addition to the volatile products, substantial amounts of a yellowish, non-volatile solid are also formed from the outset, preferentially on the lower surfaces of the reaction vessel (see later).

The reaction profile in Figure 1 is typical of thermolyses at the higher temperatures and pressures, under which conditions the reaction is very rapid and, with the possible exception of $B_{10}H_{14}$, the volatile products appear simultaneously from time t = 0. However, for thermolyses at the lower temperatures and pressures, in which the extended time-scale makes it possible to follow the initial stages of the reaction in greater detail, it is apparent that the reaction profiles for the formation of hydrogen and B_5H_{11} are quite different from those for B_2H_6, B_6H_{12}, and $B_{10}H_{14}$. This is illustrated in Figure 2, which shows the build-up of the volatile products during the first 200 min of a thermolysis of B_4H_{10} (p_0 = 3.89 mmHg) at 313.4 K. Hydrogen and the main volatile borane, B_5H_{11}, are formed without any

Table 2. Initial-rate data for thermolysis of B_4H_{10}*

T/K	$p_0(B_4H_{10})$/ mmHg	$10[B_4H_{10}]_0$/ mol m^{-3}	$-10^6(d[B_4H_{10}]/dt)_0$/ mol m^{-3} s^{-1}	$10^6(d[H_2]/dt)_0$/ mol m^{-3} s^{-1}	$10^6(d[B_5H_{11}]/dt)_0$/ mol m^{-3} s^{-1}
313.4 ± 0.2	0.86	0.44	0.76	—	0.26
	1.00	0.51	0.86	0.77	0.34
	2.48	1.27	—	2.64	—
	3.89	1.99	3.31	2.70	1.43
	4.55	2.33	5.09	4.03	—
	5.44	2.78	4.20	6.44	—
	5.63	2.88	—	4.40	—
	7.36	3.77	8.17	6.21	3.03
	7.44	3.81	—	7.82	—
	8.70	4.45	—	6.38	—
	9.55	4.89	8.43	9.10	3.62
	38.69	19.79	30.22	30.47	18.33
325.6 ± 0.8	1.14	0.56	5.31	5.94	—
	2.38	1.17	9.73	10.46	—
	4.29	2.11	18.01	22.01	—
	5.45	2.68	19.11	22.90	—
	7.92	3.90	27.04	31.86	12.10
	10.68	5.26	33.96	43.37	19.87
332.6 ± 0.4	1.16	0.56	7.4	10.7	—
	1.62	0.78	13.3	15.0	—
	2.38	1.15	17.1	24.4	—
	3.71	1.79	26.5	41.5	12.53
	5.49	2.65	29.0	42.2	—
	6.45	3.11	52.3	56.0	—
	7.60	3.66	71.4	78.9	23.21
	10.26	4.95	77.6	89.0	—
	12.36	5.96	—	112.1	—
351 ± 1	0.98	0.45	43.7	85.7	14.80
	2.50	1.14	102.8	200.9	—
	3.06	1.40	104.4	215.4	49.48
	3.11	1.42	111.9	184.2	62.20
	3.88	1.77	131.7	—	—
	7.65	3.49	225.1	423.2	162.4
	10.23	4.67	320.5	—	—
	10.66	4.86	373.7	705.7	276.0
	15.23	6.96	527.5	900.2	—

* In some cases, because of instrumental malfunction, it was not always possible to record both the borane and hydrogen data.

Table 3. Reaction orders (n) obtained from initial-rate studies on the thermolysis of B_4H_{10}

T/K	$n_{B_4H_{10}}$ [a]	n_{H_2} [b]	$n_{B_5H_{11}}$ [c]
313.4 ± 0.2	0.99 ± 0.07	0.98 ± 0.06	1.11 ± 0.02
325.6 ± 0.8	0.83 ± 0.03	0.89 ± 0.05	—
332.6 ± 0.4	1.05 ± 0.09	0.97 ± 0.05	—
351 ± 1	0.89 ± 0.04	0.86 ± 0.05	1.21 ± 0.06

Reaction orders (with respect to the concentration of B_4H_{10}) determined from: [a] rate of consumption of B_4H_{10}; [b] rate of production of hydrogen; [c] rate of production of B_5H_{11}.

observable induction period, *i.e.* the maximum rates of formation occur at time $t = 0$. For B_6H_{12}, however, this maximum occurs after *ca.* 45 min, and for B_2H_6 and $B_{10}H_{14}$ after *ca.* 80 min.

If the pressure is reduced still further, the induction periods become even longer; for example, with an initial B_4H_{10} pressure of 1 mmHg the maximum rate of formation of B_2H_6 is delayed for a period of *ca.* 180 min. These effects are reproducible and are not artefacts of the analytical method. The mechanistic implications of these observations are discussed in a later section.

Reaction Order and Rate Constants.—From Figure 1 it is clear that the reaction mixture rapidly becomes very complex. After less than one half-life (*ca.* 15 min at $T = 351$ K) appreciable quantities of H_2 and B_5H_{11} are present and the reaction can no longer be regarded as a simple thermolysis of pure B_4H_{10}. We have therefore chosen to determine the reaction order by the initial-rate (or differential) method, which minimizes the effects of interference from reaction products.

Initial rates of consumption of B_4H_{10} and production of H_2 were measured at four temperatures in the range 313.4—351.0 K and at numerous pressures in the range 0.86—38.69 mmHg. The results are recorded in Table 2 and given in the form of a composite log–log plot in Figure 3. The slopes of the lines of best fit from a least-squares analysis of the data are given in Table 3, and are consistent with an experimental order of unity (with respect to the concentration of B_4H_{10}) over the entire range of temperature and pressure covered. The orders obtained at 313.4 K, $n_{B_4H_{10}} = 0.99 \pm 0.07$ and $n_{H_2} = 0.98 \pm 0.06$, are particularly noteworthy, as the data span a wider pressure range than that covered at any of the other temperatures, and are therefore likely to give the most reliable overall result. In this respect it is important to note that there are no indications at this temperature, or indeed at any of the temperatures studied, of the

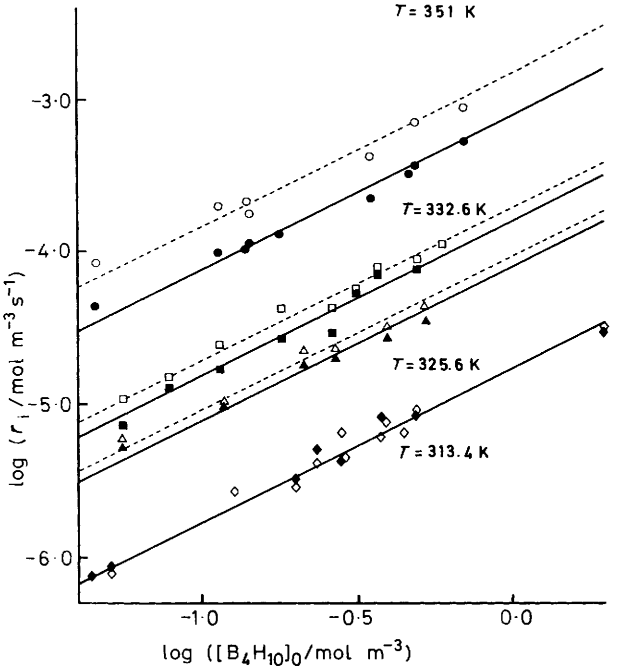

Figure 3. Plots of the log of the initial rate (r_i) *versus* the log of the initial concentration of B_4H_{10}. Filled symbols and solid lines refer to tetraborane consumption, open symbols and broken lines to hydrogen production. The slopes of the lines of best fit are given in Table 3. This figure shows lines of best fit of slope unity, the intercept in each case being the log of the mean value of the first-order rate constants. At T = 313.4 K the hydrogen and B_4H_{10} data fall on the same line of best fit

mixed or $\frac{3}{2}$-order behaviour claimed by Bond and Pinsky* to be predominant below 60 °C at pressures under 100 mmHg.

Initial rates of production of B_5H_{11} are also included in Table 2 and, as indicated in Figure 4, plots of the log of the initial rate *versus* the log of the initial concentration of B_4H_{10} yield excellent linear dependences. The slopes of the lines of best fit, 1.11 ± 0.02 and 1.21 ± 0.06 are suggestive of first-order behaviour, but the slight deviation from unity in each case may have significance, as discussed later.

The mean values, at each temperature, for the observed first-order rate constants for B_4H_{10} consumption, H_2 production, and B_5H_{11} production are listed in Table 4. It is apparent that the rate constant for hydrogen production decreases with decrease in temperature relative to that for B_4H_{10} consumption, until at T = 313.4 K the two are equal. By contrast the values of the ratio $k_{1,B_5H_{11}}/k_{1,B_4H_{10}}$ at the three lower temperatures are in remarkably close agreement (0.43 ± 0.13, *ca.* 0.44, and *ca.* 0.44). The value at T = 351 K is marginally higher (0.57 ± 0.17), but this may well be because the initial rate of B_4H_{10} consumption was underestimated at this temperature (see later). The true value of $k_{1,B_4H_{10}}$ at T = 351 K is believed to be near 102 × 10^{-5} s^{-1}, in which case $k_{1,B_5H_{11}}/k_{1,B_4H_{10}}$ = 0.43, in excellent agreement with the values at the lower temperatures. As will become apparent later, this observation, that the *initial* reaction produces nearly 0.5 mole of B_5H_{11} per mole of B_4H_{10}, has important mechanistic implications. Moreover, as only minor amounts of other volatile boranes are produced in the very early stages (see Figure 2), it is evident that substantial amounts of non-volatile materials are also formed, and this is considered

Table 4. First-order rate constants for thermolysis of B_4H_{10}[a]

T/K	$10^5k_{1,B_4H_{10}}$/s^{-1} [b]	$10^5k_{1,H_2}$/s^{-1}	$10^5k_{1,B_5H_{11}}$/s^{-1}
313.4 ± 0.2	1.73 ± 0.25	1.74 ± 0.24	0.74 ± 0.11
325.6 ± 0.8	7.7 ± 1.1	9.1 ± 1.0	~3.4
332.6 ± 0.4	15.4 ± 2.4	19.3 ± 2.7	~6.7
351 ± 1	77 ± 9	148 ± 24	44 ± 8

[a] The data listed are mean values of initial rate constants evaluated from the expressions; $k_{1,B_4H_{10}} = -(d[B_4H_{10}]/dt)_0/[B_4H_{10}]_0$, $k_{1,H_2} = (d[H_2]/dt)_0/[B_4H_{10}]_0$, and $k_{1,B_5H_{11}} = (d[B_5H_{11}]/dt)_0/[B_4H_{10}]_0$. [b] These values are believed to be related to the elementary rate constant k_1 for reaction (1), *i.e.* elimination of H_2 from B_4H_{10}, by the expression $k_{1,B_4H_{10}} = 2k_1$ (see Discussion section).

Table 5. First-order rate constants at T = 313.4 K*

$p_0(B_4H_{10})$/ mmHg	$10^5k_{1,B_4H_{10}}$/s^{-1}	$10^5k_{1,H_2}$/s^{-1}	$10^5k_{1,B_5H_{11}}$/s^{-1}
0.86	1.73	—	0.59
1.00	1.69	1.51	0.67
2.48	—	2.08	—
3.89	1.44	1.64	0.72
4.55	2.18	1.73	—
5.44	1.51	2.32	—
5.63	—	1.53	—
7.36	2.17	1.65	0.80
7.44	—	2.05	—
8.70	—	1.43	—
9.55	1.72	1.86	0.74
38.69	1.53	1.54	0.93

* The values listed were evaluated from the expressions given in footnote *a* of Table 4.

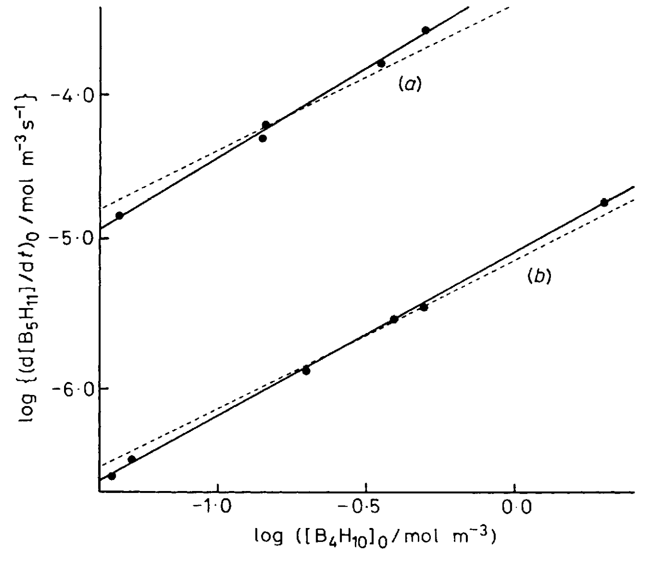

Figure 4. Plots of the log of the initial rate of production of B_5H_{11} *versus* the log of the initial concentration of B_4H_{10}: (*a*) at T = 313.4, (*b*) at T = 351 K. The solid lines represent the best least-squares fits to the data and have slopes of (*a*) 1.11 ± 0.02, and (*b*) 1.21 ± 0.06. The broken lines represent the best-fit lines of slope unity

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* Bond and Pinsky[5] cited an earlier study as being consistent with $\frac{3}{2}$-order kinetics. The raw data have been reproduced by Faust[6] and attributed to Stock; however, the reference given appears to be incorrect and we have not been able to locate the original report of this work. In any case the work appears to have been limited in scope and, in view of the fact that B_5H_9 is reported as being the main product, is probably sufficiently unreliable to be discounted.

Table 6. First-order rate constants for thermolyses of B_4H_{10} (p_0 = 5.0 mmHg) in a packed and unpacked spherical bulb at T = 348.1 K

Condition of vessel	$10^4k_{1,B_4H_{10}}/s^{-1}$	$10^4k_{1,H_2}/s^{-1}$	$10^4k_{1,B_5H_{11}}/s^{-1}$	$k_{1,B_5H_{11}}/k_{1,B_4H_{10}}$
Packed, unconditioned	9.70	9.38	3.81	0.39
Packed, conditioned	9.63	7.16	3.84	0.40
Unpacked, conditioned	9.13	9.91	3.82	0.42

Table 7. Stoicheiometry of the non-volatile solid at t = 0 and t = 200 min, in thermolyses at T = 313.4 K*

	x in BH_x	
$p_0(B_4H_{10})$/mmHg	t = 0	t = 200 min
0.86	1.85	2.17
1.00	1.82	2.14
3.89	1.79	1.96
7.36	1.73	1.92
9.55	1.78	1.47
38.69	1.61	1.39
$\bar{x}$	1.76 ± 0.08	1.84 ± 0.31

* On average, in these six thermolyses, 17.0 ± 2.1% of the initial amount of B_4H_{10} was consumed within 200 min.

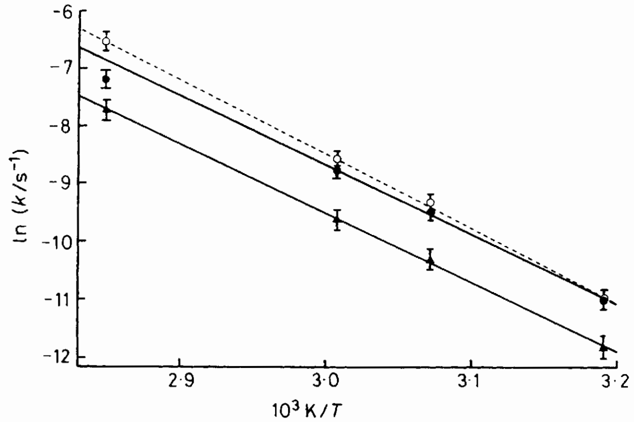

Figure 5. Arrhenius plot for the thermolysis of B_4H_{10}: mean values of the first-order rate constants (●) $k_{1,B_4H_{10}}$, (○) k_{1,H_2}, and (▲) $k_{1,B_5H_{11}}$ recorded in the present study

in the next section. More detailed information about the individual thermolyses at T = 313.4 K (Table 5) suggests that $k_{1,B_5H_{11}}$ may in fact be pressure-dependent. The wide range of pressures covered at this temperature reveals a discernible trend in the B_5H_{11} data, not paralleled in the values for $k_{1,B_4H_{10}}$ and k_{1,H_2}. This would account for the slight deviation from unity in the observed order for the production of B_5H_{11}, which was evaluated from this set of data.

To investigate the possible effect of an increased surface area on the reaction, two thermolyses were carried out at T = 348.1 K in a spherical reaction vessel packed with Raschig rings so as to increase the surface area : volume ratio by a factor of 33. In the first of these the vessel and its contents had not previously been exposed to boranes, and in the second the surfaces were conditioned as described in the Experimental section. Initial first-order rate constants are given in Table 6, where they are compared with values for a control experiment in an unpacked bulb. From these results it is clear that the *initial* rate of consumption of B_4H_{10} is essentially unaffected by a 33-fold increase in the surface area : volume ratio or by the nature of the surface, and that the rate-limiting step is therefore (as previously suggested[1,2]) a homogeneous gas-phase reaction. The rates of production of the various volatile components are also essentially unaffected; for example, the values of the ratio $k_{1,B_5H_{11}}/k_{1,B_4H_{10}}$ are 0.42, 0.40, and 0.39 for the three experiments, in remarkably close agreement with those referred to above. As will become apparent later these observations have important mechanistic significance.

Stoicheiometry of the Non-volatile Solid.—On the basis of the average values at 313.4 K for the first-order rate constants $k_{1,B_4H_{10}}$ = 1.73 ± 0.25 s^{-1} and k_{1,H_2} = 1.74 ± 0.24 s^{-1} listed in Table 4, and the values for $k_{1,B_5H_{11}}$ in Table 5, it is possible to arrive at estimates for the initial stoicheiometry of the non-volatile solid. These are listed in Table 7 where they are compared with estimates at t = 200 min derived from detailed mass-balance calculations on the product analyses at T = 313.4 K. Because of the large cumulative errors involved, these values are not likely to be highly accurate and this is borne out in the large scatter in the values obtained. However, there is reasonable agreement between the average stoicheiometries of $BH_{1.76\pm0.08}$ and $BH_{1.84\pm0.31}$ obtained at t = 0 and t = 200 min, respectively, indicating that the solid is relatively stable at this temperature. Consistent with this, is the observation that at t = 200 min the average ratio of hydrogen produced to B_4H_{10} consumed, in the six thermolyses listed, was 1.02 ± 0.17; *i.e.* the same as the ratio of the initial rate constants (1.73 : 1.74) at T = 313.4 K (Table 4). As the temperature is raised, there is a progressive increase in the rate of hydrogen production relative to the rate of B_4H_{10} consumption, but no discernible change in the distribution of volatiles. This indicates clearly that the hydrogen content of the solid decreases with increase in temperature.

Activation Energies.—The first-order rate constants given in Table 4 are recorded in the form of an Arrhenius plot in Figure 5. Close inspection of this Figure suggests that one of the 12 data points (that for $k_{1,B_4H_{10}}$ at T = 351 K) is unrealistically low. This point falls off the line of best fit drawn through the other three data points for this species, which in turn runs closely parallel to the line of best fit to the B_5H_{11} data. If the suspect point is ignored in the least-square analysis, the value obtained for the activation energy, $E_{a,B_4H_{10}}$ = 99.4 ± 3.4 kJ mol^{-1}, is in very close agreement with that obtained from a least-squares analysis of the B_5H_{11} data, $E_{a,B_5H_{11}}$ = 98.8 ± 1.8 kJ mol^{-1}; the corresponding values for the pre-exponential factor are $A_{B_4H_{10}} = e^{27.2\pm1.3}$ (*ca.* 6.4 × 10^{11}) and $A_{B_5H_{11}} = e^{26.1\pm0.5}$ (*ca.* 2.3 × 10^{11}) s^{-1}. As there are good reasons for believing that $E_{a,B_4H_{10}}$ and $E_{a,B_5H_{11}}$ refer to the same activation energy (see later), it seems very probable that the values of the rate constant $k_{1,B_4H_{10}}$ at T = 351 K were underestimated. With hindsight this can be attributed to the difficulties of measuring particularly rapid initial rates, which are susceptible to problems of source conditioning and the effects of pressure- and temperature-equilibration. It would therefore appear that T = 351 K represents the upper limit for studying the thermolysis of B_4H_{10} in this pressure range by the present technique.

The overall activation energy for the production of hydrogen, given by the least-squares analysis of the data in Figure 5 (E_{a,H_2} = 107.5 ± 1.85 kJ mol^{-1}), is somewhat greater than that for B_4H_{10} consumption; the corresponding pre-exponential factor is $A_{H_2} = e^{30.3 \pm 0.6}$ (*ca.* 1.5 × 10^{13}) s^{-1}.

Discussion

Summary of Main Results.—Before discussing possible mechanisms for the initial reaction, it is convenient to summarize the main experimental findings that need to be accounted for.

(*i*) In the pressure range 0.86—38.69 mmHg, and over the temperature range 313.4—351.0 K, B_4H_{10} decomposes with first-order kinetics in a homogeneous gas-phase reaction having an overall activation energy E_a = 99.4 ± 3.4 kJ mol^{-1} and $A \approx 6.4 \times 10^{11}$ s^{-1}.

(*ii*) The main volatile products are B_5H_{11} and hydrogen; the latter appears with first-order kinetics (with respect to the concentration of B_4H_{10}), but there is a slight deviation from unity in the order for B_5H_{11} production, which may be significant.

(*iii*) In the *initial* reaction, each mole of B_4H_{10} produces, on average, 0.44 mole of B_5H_{11}; this proportion is independent of temperature, surface area:volume ratio, or the nature of the surface, but shows a slight tendency to increase with increase in initial pressure of B_4H_{10}. The remaining B_4H_{10} is converted to hydrogen and a non-volatile solid, BH_x (where $x \sim 1.76$ at 313.4 K, and decreases with increase in temperature as more hydrogen is released).

(*iv*) Other volatile boranes are also produced in the reaction, but induction periods are involved in their formation; B_6H_{12} appears before B_2H_6 and $B_{10}H_{14}$, but B_5H_9 and B_6H_{10} are not detected during the initial stages.

Mechanistic Implications.—In the past, the forward steps of the reversible routes (1a)[2,3] and (1b)[4,5] have each been put

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

$$B_4H_{10} \rightleftharpoons \{BH_3\} + \{B_3H_7\} \qquad (1b)$$

forward to explain first-order kinetics, and it has also been suggested that both might occur simultaneously.[1] Although the balance of the evidence was consistent with (1a),[7] doubts were expressed[4] about its importance, because of the reported[10] failure to observe exchange of dideuterium with B_4H_{10}. We recently removed this particular difficulty by showing that, in fact, exchange occurs readily even under mild conditions.[7] However, it has been difficult to decide whether, in addition to reaction (1a), reaction (1b) also occurs, because the highly reactive species $\{BH_3\}$ and $\{B_3H_7\}$ are likely to be generated in any case in rapid reactions subsequent to (1a). Dupont and Schaeffer[2] pointed out that there was evidence[11] to indicate that B_2H_6 reacts rapidly with $\{B_3H_7\}$ to give B_4H_{10}, and would therefore be expected to inhibit the thermal decomposition of B_4H_{10} if (1b) were a concurrent rate-determining step. Their observation that, in the co-thermolysis,[2] the consumption of B_4H_{10} was zero order in B_2H_6, therefore argued strongly against the involvement of reaction (1b). Moreover, the discovery that B_4H_{10} reacted with CO to give B_4H_8CO,[3] with an activation energy and first-order rate constant similar to those for the B_4H_{10}/B_2H_6 co-thermolysis, was convincing evidence in favour of (1a). Subsequent work of Bond and Pinsky[5] caused confusion but, as there is no evidence in the present study to substantiate their claim of a change in order below 60 °C (333.1 K), the chain mechanism proposed by them to explain $\frac{3}{2}$-order kinetics and involving (1b) as the initiation step, can therefore be discounted. Thus, in the light of the present unequivocal demonstration that B_4H_{10} decomposes with first-order kinetics, Schaeffer's earlier arguments seem incontrovertible, and there can be little doubt that (1a) is indeed the sole rate-determining step in the thermolysis.

The broad features of the observed initial reaction (both its stoicheiometry and kinetics) can now be understood if steps (2) and (3) follow step (1a) in rapid succession. Reaction (3) is

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

$$\{B_3H_7\} + \{B_3H_7\} \longrightarrow \{\text{'}B_6H_{14-2m}\text{'}\} \text{ (polymerizes)} + mH_2 \qquad (3)$$

presumed to give a volatile, transient (B_6) intermediate which then reacts readily either with itself or with further $\{B_3H_7\}$ to give a non-volatile solid. Reaction of $\{B_3H_7\}$ with the walls of the vessel is a further possibility, but this is considered to be less important as discussed later. Application of the steady-state approximation to $[\{B_3H_7\}]$ and $[\{B_4H_8\}]$ yields the expressions $-d[B_4H_{10}]/dt = 2k_1[B_4H_{10}]$ and $d[B_5H_{11}]/dt = k_1[B_4H_{10}]$ for the rate of consumption of B_4H_{10} and the rate of production of B_5H_{11} [where k_1 is the elementary rate constant for reaction (1a)]. Thus, B_5H_{11} should be produced at half the rate that B_4H_{10} is consumed, as observed experimentally (see Table 4). As no other volatile borane is observed in the initial reaction, the implication is that the $\{B_3H_7\}$ formed in reaction (2) is removed rapidly as a non-volatile solid polymer *via* reaction (3). At T = 313.4 K, when the observed rate of hydrogen production happens to equal the rate of B_4H_{10} consumption, the 'three-step' mechanism predicts a polymer stoicheiometry of $BH_{1.67}$, compared with the average stoicheiometry of $BH_{1.76 \pm 0.08}$ observed experimentally (see Table 7). As the temperature is raised, the rate of hydrogen production increases relative to the rate of B_4H_{10} consumption, and the hydrogen content of the polymer decreases. If this mechanism is correct, it is clear that for every mole of $\{B_4H_8\}$ produced in reaction (1a), an equal amount of $\{B_3H_7\}$ is generated by reaction (2). It is therefore interesting that Stafford and co-workers[12,13] observed $\{B_4H_8\}$ but failed to observe $\{B_3H_7\}$ in their 'integral-furnace' mass-spectrometric studies of the pyrolysis of B_4H_{10}. In the light of the mechanism proposed above, it is clear that this result should be interpreted *not* in terms of the non-formation of $\{B_3H_7\}$, but rather as an indication of a low steady-state concentration resulting from its rapid removal by the energetically favourable polymerization *via* reaction (3).

Though it is within experimental error, the slight discrepancy between the observed and predicted rate-constant ratio $k_{1,B_5H_{11}}/k_{1,B_4H_{10}}$ (*i.e.* 0.44 compared with 0.50) is consistent over the whole temperature range and, if real, would indicate that *ca.* 12% of the $\{B_4H_8\}$ was disappearing by some other route, or that the equivalent amount of B_5H_{11} was escaping detection by reacting further or decomposing. As B_5H_{11} is known[9] to be relatively stable under the present conditions, its rapid or extensive decomposition can be ruled out; indeed, B_2H_6, its main thermolysis product, is not observed during the period that the initial rates were measured at T = 313.4 K. Neither can the incipient reaction (4) account for this amount of material in the initial stages. However, it can be shown, on the basis of a standard steady-state treatment, that the inclusion of reaction (5) as a *minor* route for the removal of $\{B_4H_8\}$ as polymer, accounts not only for this discrepancy, but also for the

$$\{B_4H_8\} + B_5H_{11} \longrightarrow B_6H_{12} + \{B_3H_7\} \qquad (4)$$

$$\{B_4H_8\} + \{B_4H_8\} \longrightarrow \{\text{'}B_8H_{16-2n}\text{'}\} \text{ (polymerizes)} + nH_2 \qquad (5)$$

observed pressure dependence of the rate constant for the production of B_5H_{11} (Table 5), which in turn leads to the slight deviation from unity in the order. This accumulation of evidence therefore leads one to believe that all of these minor effects are in fact genuine. If this is indeed so, then it can be argued that the present results show conclusively that reaction (1a) is the sole route for the decomposition of B_4H_{10}. Thus, although reaction (1b) followed rapidly by reactions (6) and (3) would equally well account for the main kinetic and stoicheiometric features, there appears to be no parallel route to compete with reaction (6) for the removal of $\{BH_3\}$. The forward reaction (7), which is known to have zero activation energy,[14]

$$\{BH_3\} + B_4H_{10} \longrightarrow B_5H_{11} + H_2 \qquad (6)$$

$$2\{BH_3\} \rightleftharpoons B_2H_6 \qquad (7)$$

manifestly does not occur because B_2H_6 is absent from the *initial* reaction products. It is therefore difficult [on the basis of the $\{B_3H_7\}$ route (1b)] to explain the discrepancy between the predicted and observed initial ratio of rate constants, and the observed pressure dependence of $k_{1,B_5H_{11}}$. Indeed, it is possible that the absence of B_2H_6 in the initial stages is, by itself, sufficient evidence to rule out reaction (1b). Whether or not this is so depends, in fact, on the extent to which reaction (6) would compete with reaction (7) for the $\{BH_3\}$ produced in (1b), and such detailed information is at present lacking.

An important conclusion that can be drawn from the present work is that $\{B_3H_7\}$, whether generated by reaction (1b) or reaction (2), does *not* react with B_4H_{10} to give B_5H_{11} and B_2H_6; neither does it react to any significant extent with $\{B_4H_8\}$ to give B_5H_9 and B_2H_6, or with itself to give B_6H_{12} and H_2, or $\{B_4H_8\}$ and B_2H_6.

These various reactions have been invoked in the past,[4] but the observation of induction periods in the formation of B_2H_6 and B_6H_{12} shows that they are not favoured routes under the present conditions. Likewise, the proposed self-reactions of $2\{B_4H_8\}$ to form either B_2H_6 and B_6H_{10},[4,15] or $\{B_3H_7\}$ and B_5H_9[4] are also ruled out and it is unlikely that the self-reactions of $\{B_4H_8\}$ and $\{B_3H_7\}$ invoked by Shore and co-workers[16] to explain the low-temperature (−30 to 0 °C), high-yield syntheses of B_5H_{11} and B_4H_{10} are relevant under the present experimental conditions. All the evidence suggests that these non-isolable species *do* react with themselves, but only to give non-volatile polymeric solids. The formation of polymer from $\{B_4H_8\}$ has been proposed previously on the basis of shock-tube experiments,[17] and the rapid polymerization of low-molecular weight fragments in the *gas phase* has been surmised previously from the observation (confirmed in the present work) that the solids settle predominantly on the lower portions of the reaction vessel.[5] Further confirmation that $\{B_4H_8\}$ (and presumably $\{B_3H_7\}$ also) does *not* polymerize at the walls comes from the observation that the rate-constant ratio $k_{1,B_5H_{11}}/k_{1,B_4H_{10}}$ is essentially independent of the nature of the surface or the surface area : volume ratio. In the proposed 'three-step' mechanism, the minor route (4) for the removal of $\{B_4H_8\}$ is seen to be in competition with reaction (2), which leads to B_5H_{11}. If this minor route were a heterogeneous (wall) reaction, then a 33-fold increase in the surface area : volume ratio should increase its importance dramatically at the expense of the production of B_5H_{11}, but this does not happen. This body of evidence, coupled with the late appearance of B_6H_{12} and $B_{10}H_{14}$ in the present reaction (see Figure 2), also emphasizes that the solids do not arise, as was once commonly imagined, solely as a result of progressive increase in cluster size or cluster catenation *via* routes involving the higher volatile boranes.

The build up of volatile boranes other than B_5H_{11} in the thermolysis is seen as the result of reactions subsequent to those involved in the *initial* stages, as appreciable induction periods are involved. The most probable route to B_6H_{12} appears to be reaction (8). The analogous reaction of B_5H_{11} with $\{B_3H_7\}$

$$\{B_4H_8\} + B_5H_{11} \longrightarrow B_6H_{12} + \{B_3H_7\} \qquad (8)$$

seems less likely, as this would produce B_2H_6 in equal proportions to, and simultaneously with B_6H_{12}, which is not consistent with the observations. Diborane(6) probably results from the decomposition of B_5H_{11}, followed by $\{BH_3\}$ abstraction, *i.e.* reactions (9)—(11). In this way the step-wise

$$B_5H_{11} \longrightarrow \{B_4H_8\} + \{BH_3\} \qquad (9)$$

$$\{BH_3\} + B_5H_{11} \longrightarrow B_2H_6 + \{B_4H_8\} \qquad (10)$$

$$\{BH_3\} + B_4H_{10} \longrightarrow B_2H_6 + \{B_3H_7\} \qquad (11)$$

build-up in boron content is continued. Long[4] has proposed that $B_{10}H_{14}$ may be formed at low temperatures *via* the intermediate formation of B_9H_{15} from the reaction between $\{B_4H_8\}$ and B_5H_{11}. If this were in fact the main route, one might expect to see $B_{10}H_{14}$ being formed from the outset, because the concentration of B_5H_{11} builds up rapildy. In the event, $B_{10}H_{14}$ is formed only after an induction period, and not before the concentration of B_6H_{12} has built up; this suggests that the latter may be involved as an intermediary.

Comparison with Previous Kinetic Studies.—As mentioned earlier, the present work has shown no evidence for the mixed $\frac{3}{2}$/first-order behaviour reported in the most recent and extensive study of this thermolysis by Bond and Pinsky.[5] However, it is now clear that the integration (order-plot) method used in that work is completely unsuited to an analysis of this problem. For example, at $T = 60$ °C, B_4H_{10} decomposes to the extent of *ca.* 50% in 1 h, with the production of an equivalent amount of hydrogen, which is known[1] to inhibit the reaction. However, this effect seems to have been ignored by Bond and Pinsky,[5] who analysed their data over periods of up to *ca.* 5 h. It is also interesting to note that B_6H_{12} was observed only at very high pressures (⩾73 mmHg) and that $B_{10}H_{14}$ was not detected in their work.

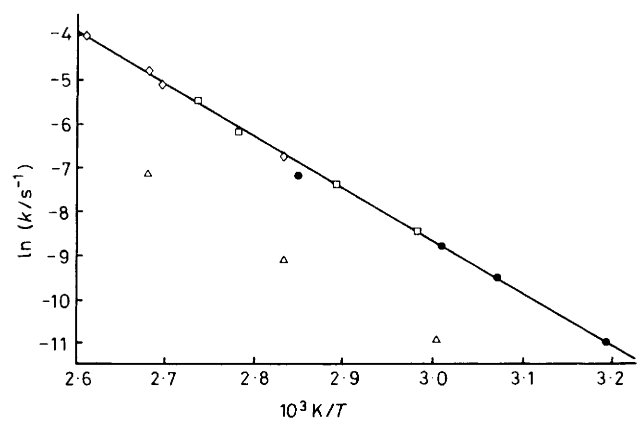

Figure 6. Comparisons of rate constants for B_4H_{10} consumption obtained in this work (●), with those obtained by Pearson and Edwards[1] (△), and by Schaeffer and co-workers for the co-thermolysis of B_4H_{10} with B_2H_6[2] (□) and CO[3] (◇). The solid line represents the least-squares best fit to our own data combined with that reported by Dupont and Schaeffer[2] for the B_4H_{10}/B_2H_6 co-thermolysis

There have been only three other kinetic studies of note involving B_4H_{10},[1-3] all of which have been consistent with first-order kinetics. The first-order rate constants from these studies are compared with those of the present work in the Arrhenius plot in Figure 6. Rather surprisingly, our rate constants for the consumption of B_4H_{10} in the *self-reaction* are seen to fall on the *same* straight line as those recorded by Schaeffer and co-workers for *co-thermolysis* reactions of B_4H_{10} with B_2H_6[2] and CO,[3] respectively, but on a quite different line from the data of Pearson and Edwards[1] for the thermolysis of B_4H_{10} alone. However, the values obtained for the activation energy in the three studies, $E_{a,B_4H_{10}} = 101.7$,[2] 102.8,[3] and 97.9[1] kJ mol^{-1}, respectively, are in very good agreement with one another, and with the value of 99.4 ± 3.4 kJ mol^{-1} recorded in the present study.

Schaeffer and co-workers found that their co-thermolyses were zero order in the co-reactants B_2H_6[2] and CO,[3] and used the close agreement between their two pieces of work to conclude that the reaction intermediate in each case was probably the same, namely $\{B_4H_8\}$. The results of the present study confirm suspicions[2] that the rate constants reported by Pearson and Edwards[1] were in error by some two orders of magnitude, and appear to be entirely consistent with Schaeffer's views. There is, however, a slight inconsistency in the arguments used by Schaeffer and co-workers[2,3] which ought to be considered. Thus, the two-step mechanism which they proposed to explain the B_4H_{10}/B_2H_6 co-thermolysis, *i.e.* reaction (1a) followed by reaction (12), does not by itself account for

$$\{B_4H_8\} + B_2H_6 \longrightarrow B_5H_{11} + \{BH_3\} \qquad (12)$$

$$2B_4H_{10} + B_2H_6 \rightleftharpoons 2B_5H_{11} + 2H_2 \qquad (13)$$

the observed stoicheiometry (13). This requires a third step involving the reactive intermediate $\{BH_3\}$. In fact there are three possible fates for the $\{BH_3\}$ in the initial stages of this reaction that are consistent with the observed stoicheiometry, namely reaction (6), reaction (7), and reaction of $\{BH_3\}$ with B_4H_8 to give B_5H_{11}. However, a steady-state analysis indicates that only the first of these three options predicts the observed agreement (see Figure 6) between the overall rate constants reported in this study for the thermolysis of B_4H_{10} alone, and those reported by Dupont and Schaeffer[2] for the B_4H_{10}/B_2H_6 co-thermolysis (*i.e.* $-d[B_4H_{10}]/dt = 2k_1[B_4H_{10}]$); the others predict a rate of half this value. Thus, if the observed agreement is meaningful, the combined results of these two pieces of work lead to the conclusion that reaction (6) is indeed the third step in the mechanism for the co-thermolysis. It is worth noting that $\{B_3H_7\}$ is not featured in this three-step co-thermolysis mechanism and, in the light of our proposal that this reactive species is the major source of polymer in the B_4H_{10} thermolysis, the *absence* of non-volatile solids in the B_4H_{10}/B_2H_6 co-thermolysis is thereby explained.

Finally, on the basis of the proposed[3] mechanism for the B_4H_{10}/CO co-thermolysis, namely reaction (1a) followed by the rapid reaction of $\{B_4H_8\}$ with CO to give B_4H_8CO, a steady-state analysis predicts the rate of decomposition to be given by $-d[B_4H_{10}]/dt = k_1[B_4H_{10}]$. This is half the rate predicted for the B_4H_{10}/B_2H_6 co-thermolysis, and half the value observed experimentally. It therefore seems that the excellent agreement observed in the two co-thermolysis studies may have been fortuitous. There is, however, a plausible explanation. Thus, Spielman and Burg[18] have also reported rate constants for the co-thermolysis of B_4H_{10} and CO, which (though not planned as accurate rate measurements) happened to agree quite well with those of Brennan and Schaeffer.[3] However, the yield of B_4H_8CO is these experiments averaged only *ca.* 50%, the difference being attributed to a parallel decomposition of B_4H_{10}. If, as is likely, similar difficulties were encountered by Brennan and Schaeffer, then their reported rate constants are probably a factor of 2 greater than the true rate constants for the co-thermolysis reaction. Indeed, no claim was made that the values were highly precise.

The compatibility of the data recorded in the present study with those for the B_4H_{10}/B_2H_6 co-thermolysis gives confidence in the proposed mechanisms, and is particularly gratifying because the two sets of data jointly span a much wider range of temperature than that covered by each set individually. A combined analysis is therefore likely to yield more accurate Arrhenius parameters for the overall process. The line of best fit from such a least-squares treatment is shown in Figure 6, and yields a value for the activation energy of $E_{a,B_4H_{10}} = 99.2 \pm 0.76$ kJ mol^{-1} with a pre-exponential factor, $A_{B_4H_{10}} = e^{27.1 \pm 0.3}$ (*ca.* 6.0 × 10^{11}) s^{-1}. On the basis of the assumed mechanisms this overall activation energy will refer to reaction (1a), *i.e.* to the elimination of H_2 from B_4H_{10}. The subsequent rapid reactions involving the unstable intermediates are assumed to have zero or low activation energy. Likewise, the observed rate constants $k_{1,B_4H_{10}}$ are believed to be related to the elementary rate constant k_1 for reaction (1a) by the expression $k_{1,B_4H_{10}} = 2k_1$.

Conclusions

An assessment of the present results, together with all other relevant evidence, indicates that in the temperature range 40.3—92.5 °C (313.4—365.6 K), B_4H_{10} decomposes in a first-order, homogeneous gas-phase reaction, with an activation energy $E_{a,B_4H_{10}} = 99.2 \pm 0.76$ kJ mol^{-1} and a pre-exponential factor $A_{B_4H_{10}} \sim 6.0 \times 10^{11}$ s^{-1}. The stoicheiometry of the initial reaction is approximately as given below, where x depends on

$$B_4H_{10} \longrightarrow 0.44\ B_5H_{11} + 1.8\ BH_x\ (\text{solid}) + (2.58 - 0.9x)H_2$$

temperature. The *initial* rate-limiting step has been established as the elimination of H_2 from B_4H_{10} to generate the fugitive species $\{B_4H_8\}$, which then reacts rapidly with B_4H_{10} to give B_5H_{11} and $\{B_3H_7\}$. The observation of an induction period in the formation of B_2H_6 eliminates the possibility that $\{B_3H_7\}$ reacts also to give B_5H_{11}, and the absence of any other volatile borane in the initial reaction implies that $\{B_3H_7\}$ must instead undergo rapid polymerization. To account for the observed initial stoicheiometry a minor proportion (*ca.* 12%) of the $\{B_4H_8\}$ is also required to polymerize and this reaction is shown to occur in the gas phase rather than at the walls. In the past it has been proposed that, under thermolysis conditions in the gas phase, these intermediates react either with themselves or with one another to give volatile boranes, but on the basis of the present work this now seems unlikely.

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