

Kinetics and mechanism of the thermolysis and photolysis of binary boranes

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Abstract - The mechanisms by which gaseous boron hydrides so readily interconvert and build up into larger clusters has excited considerable academic and industrial interest for several decades. This paper describes recent progress that has been made in unravelling this complex series of interconversion reactions. Initial reaction rates have been studied mass spectrometrically to obtain rate equations, orders of reaction and energies of activation. Detailed and continuous product analysis for H₂ and all the volatile boranes formed, coupled with a study of cothermolysis reactions of selected pairs of boranes gives further insight into the processes occurring. Crucial aspects of the thermolysis of B₂H₆, B₄H₁₀, B₅H₁₁, and B₆H₁₀ are discussed, as are the effects of added H₂ and the cothermolysis of B₆H₁₀ with alkenes. The final section presents data on the UV absorption spectra and photolytic stability of eight volatile boranes and the reaction kinetics of B₆H₁₀ photolysis.

INTRODUCTION

The facile interconversion of the binary boranes in the gas phase at room temperature or slightly above has excited attention from the earliest days of boron hydride chemistry (ref.1). The intriguing ability of the smaller boranes such as B₂H₆, B₄H₁₀, and B₅H₁₁ to interconvert by reaction with themselves and with each other, and their ability to aggregate further into larger and more complex borane clusters has been a dominant (and particularly useful) feature of their chemistry. Indeed, the reactions occurring in gaseous mixtures of boron hydrides probably comprise one of the most complex sequences of interconnected reactions to have yet been studied in any detail in the whole of chemistry. Progress has been slow, not only because of the inherent complexity of the system, but also because of the difficulty of handling these highly reactive air-sensitive species and because of problems associated with the quantitative analysis of products formed during the course of the reactions. The elegant series of papers by Riley Schaeffer and his group (ref. 2), the penetrating and perceptive contributions by Tom Fehlner and his group (ref. 3), and the sophisticated high-level calculations of structure variants and reaction energy-profiles by Bill Lipscomb (ref. 4) are among the landmarks of the story so far, though many others have made notable contributions. As always in the uncertain world of reaction mechanisms it has proved difficult to build a firm foundation of pertinent experimental evidence on which to construct a reliable model for the system. False starts abound, and unsuspected limitations in experimental techniques have been compounded by erroneous deductions from flawed data. However, consensus has emerged concerning the earliest stages of the thermolysis of diborane to give B₄H₁₀ as the first isolable intermediate, followed by B₅H₁₁. An alternative interpretation (ref. 5) has not found acceptance partly because some of the key pieces of experimental evidence on which the analysis was crucially dependent have subsequently been found to be incorrect (refs. 3,4,6,7).

The ready thermolytic interconversion and aggregation of the gaseous boranes should not be taken to imply that the bonds holding the atoms together are inherently weak. The opposite is the case: B-B and B-H bonds are amongst the strongest two-electron bonds known, and the great reactivity of the boranes is to be sought rather in the availability of alternative structures and vacant orbitals of similar energies. Some comparative data are in Table 1. The first pair of columns lists the heats of atomization of hydrogen, boron, and carbon on which the derived bond-enthalpy contributions in the rest of the Table ultimately depend. The value of $\Delta H^{\circ}_f, 298$ for H(g) is the enthalpy of dissociation of $\frac{1}{2}$ H₂(g), i.e. it is half the value of the single-bond dissociation energy E(H-H). Refinements which incorporate corrections for zero-point energy etc. can be neglected at this level of precision. The value for C(g) refers to the enthalpy of atomization of diamond and can be equated to E(C-C) for that material. The value for B(g) has been the subject of some uncertainty but there is now a consensus that it lies close to 566±15 kJ mol⁻¹.

Intercomparison of the next two columns of data in Table 1 shows that the two-electron-bond dissociation energies (or more properly the bond-enthalpy contributions, \bar{E} for B-B in boranes and C-C in C₂H₆ are essentially the same (≈332 kJ mol⁻¹); likewise the value of 380 kJ mol⁻¹ for BBB(3c,2e) is similar to that for \bar{E} (B-C) in BMe₃ (372 kJ mol⁻¹). The value of

TABLE 1. Some enthalpies of atomization ($\Delta H^\circ_{f,298}$) and comparative bond-enthalpy contributions, $\bar{E}(X-Y)$

$\Delta H^\circ_{f,298}/\text{kJ mol}^{-1}$ (refs.8,9)		$\bar{E}(X-Y)/\text{kJ mol}^{-1}$ (ref. 9)		$\bar{E}(X-Y)/\text{kJ mol}^{-1}$ (refs. 8,10)	
H(g)	$\frac{1}{2} \times 436$	B-B(2c,2e)	332	C-C	331 ^a
B(g)	566	BBB(3c,2e)	380	B-C	372 ^b
C(g)	356	B-H(2c,2e)	381	C-H	416
		BHB(3c,2e)	441	H-H	436

^aValue derived for C-Me in C₂H₆; this is slightly lower than the value of 356 kJ mol⁻¹ for the heat of atomization of diamond.

^bValue derived for B-Me in BMe₃; similar values are obtained from BEt₃, BBu₃, and BCy₃, but the values for B-Ph from BPh₃ and Ph₂BCl etc. are significantly higher (444, 485 kJ mol⁻¹): this has been ascribed to additional p_π-bonding (ref. 11).

381 kJ mol⁻¹ for $\bar{E}(B-H)$ is also similar, though slightly less than that for $\bar{E}(C-H)$ (416 kJ mol⁻¹) whereas the value for BHB(3c,2e) is slightly greater than the values for $\bar{E}(C-H)$ (in CH₄) and $\bar{E}(H-H)$ in H₂. It should be emphasized that the tabulated bond-enthalpy contributions for the boranes are to be regarded as approximate indications rather than as precisely determined invariant values. The reasons for this have been fully discussed, most recently in ref. 7. In particular there are insufficient experimental (or theoretically computed) data to establish the transferability of bond-enthalpy parameters from one borane to another. Indeed, the known substantial variability of B-B, B-H, and BHB interatomic distances in the boranes almost certainly implies some variability in the bond-enthalpy terms in the various borane clusters. For example, the experimentally observed range of B-B distances in binary boranes (from 160 to 200 pm) might well reflect a decrease by more than a factor of 2 (to 40%) in the corresponding B-B bond-enthalpy contributions (ref. 12). The data in Table 1 do, however, establish the robustness of the various interatomic linkages in borane clusters.

In seeking to extend our understanding of the reactions occurring during the mild thermolysis of gaseous boron hydrides we have developed a mass-spectrometric method of monitoring separately both the evolution of dihydrogen and the growth and decay of all volatile boranes in the system without disturbing the course of the reaction (refs. 13, 14). By studying the initial rates of reaction over a range of temperature and pressure it has been possible to derive rate equations, and activation energies. Moreover, the detailed and continuous product analysis as a function of time, coupled with a study of several cothermolyses of selected boranes, gives further insight into the processes occurring. In the following section, results on the thermolysis of B₂H₆ will be briefly reviewed. This will be followed by more substantial sections on the thermolysis of B₄H₁₀, B₅H₁₁ and B₆H₁₀ alone, and their cothermolysis with dihydrogen (or deuterium) and other boranes. The cothermolysis of B₆H₁₀ with alkenes is also discussed. The paper ends with a section describing some preliminary studies on the photolytic reactions of boranes.

THERMOLYSIS OF DIBORANE

The thermal decomposition of B₂H₆ was first studied kinetically in 1951 (ref. 15) and since then there have been numerous independent studies of the system (see references cited in ref. 5, and also refs. 2j, 3e, 13, 16-19). At various times the derived order of the reaction has been thought to be $\frac{1}{2}$, 1, $\frac{3}{2}$, 2, $\frac{5}{2}$, or variable, but there is now general acceptance that, for the homogeneous gas-phase thermolysis of B₂H₆ in the pressure range of 10-760 mmHg and the temperature range 50-200 °C, the order of the initial stages of the reaction is $\frac{3}{2}$. This suggests that a triborane species is involved in the rate-determining step and the currently favoured mechanism envisages a three-step process:



The dissociation equilibrium (1) generates the reactive intermediate {BH₃}; this reacts with more B₂H₆ (step 2) to generate {B₃H₉} which then loses dihydrogen in the rate-determining step (3). Theoretically-calculated reaction profiles have raised the possibility that the formation of {B₃H₉} by step (2) rather than its decomposition by step (3) is the rate-determining process (ref. 4c) but this can be discounted on the cogent grounds that under the experimental conditions obtaining during the thermolysis of B₂H₆, the 'observed' rate of (2) is some 10³-times faster than that of reaction (3) (ref. 3e). There is now also good experimental evidence for the reactive intermediates {BH₃} and {B₃H₇} under appropriate conditions (refs. 3, 16, 20).

We have reinvestigated this system (ref. 21) primarily to obtain a reliable set of comparative rate data for use in subsequent cothermolysis work and to check the order and activation energy of the initial reaction with our own mass-spectrometric techniques. In agreement with earlier studies, the major products of the thermolysis of diborane at temperatures between 120-150 °C were found to be H₂, B₅H₁₁, B₅H₉, and B₁₀H₁₄ together with smaller amounts of B₄H₁₀ and traces of B₆H₁₀, B₆H₁₂, B₈H₁₂, and B₉H₁₅. There was no evidence for heptaboranes or B₂₀H₂₆ under these conditions. Reaction orders (determined from initial rates) both for B₂H₆ loss and H₂ production were close to 3/2. From the B₂H₆ data the activation energy E_A was 92.3±6.6 kJ mol⁻¹ and the preexponential factor A was 1.58x10⁸ m³/2 mol^{-1/2} s⁻¹. The corresponding Arrhenius parameters from the initial rates of H₂ production were somewhat higher (E_A = 113.0±7.3 kJ mol⁻¹ and A = 3.08x10¹⁰ m³/2 mol^{-1/2} s⁻¹) possibly because the H₂ data measure not only the homogeneous gas-phase reaction but also a contribution from the heterogeneous decomposition of the solid hydride deposited on the surface of the reaction vessel.

Added H₂ is known to inhibit the decomposition of B₂H₆ (ref. 15a) and to alter the product distribution in favour of volatile boranes (ref. 15c). This inhibition is expected from the form of the rate-determining step (3) above and we have begun a quantitative evaluation of the effect. For example, the initial rate of decomposition of B₂H₆ at 3.5 mmHg and 150 °C is decreased by a factor of 3.4 in the presence of a 14-fold excess of H₂. Further quantitative work is planned in this area.

THERMOLYSIS OF B₄H₁₀ AND ITS EXCHANGE WITH D₂

There is now little doubt that B₄H₁₀ is the first isolable species in the thermolysis of B₂H₆ (ref. 2c). It is formed via reaction (4), though under normal thermolytic conditions



it is itself too unstable to be readily observed. Its thermolysis, like that of B₂H₆, has been the subject of numerous studies (refs. 2a, 2e, 5, 22-25) but there has been controversy on almost every aspect of its kinetics and mechanism of decomposition (see ref. 6 for detailed references). An early kinetic study (ref. 22) suggested that B₄H₁₀ might decompose by two simultaneous unimolecular paths (5a and 5b):



Subsequently there was an accumulation of mass-spectrometric, kinetic, and chemical evidence (summarized in ref. 6) in favour of (5a) as the initial step in the decomposition, but this was offset by isotope-exchange studies which purported to establish the alternative route (5b). Most disconcertingly, the apparent absence of H/D exchange between B₄H₁₀ and D₂ (ref. 26) led to the rejection of (5a) as an acceptable reaction step in the thermolytic decomposition of B₄H₁₀ (refs. 5, 26).

An early attempt to resolve this discrepancy (ref. 27) was inconclusive, but we have subsequently been able to demonstrate (ref. 6) unequivocally that a mixture of stoichiometry B₄H₁₀:3D₂ undergoes rapid and extensive exchange at 42 °C (a temperature at which the rate of thermal decomposition of B₄H₁₀ itself in the presence of hydrogen is immeasurably small). The possibility that the exchange might occur via reaction (5b) in conjunction with the reverse of reaction (3), i.e. {B₃H₇} + D₂ → {B₃H₇D₂}, can be ruled out at these temperatures since the subsequent decomposition of the postulated isotopomer of {B₃H₉} is the rate-determining step (3) in the decomposition of B₂H₆ which does not occur appreciably below 100 °C. Reaction (5a) is therefore established as the sole (or vastly predominant) initial step in the thermolysis of B₄H₁₀. This conclusion, which is entirely consistent with Riley Schaeffer's earlier views on this system, is however at odds with another more recent study on the thermolysis of B₄H₁₀ which has been interpreted in terms of a 3/2-order process predominant below 60 °C and involving reaction (5b) as the initiating step in a speculative chain mechanism (ref. 23). We therefore undertook a detailed reexamination of the thermolysis of B₄H₁₀ in the pressure range 0.9-39 mmHg and at temperatures in the range 40-78 °C (ref. 25).

The main volatile products of the thermolysis of B₄H₁₀ under these conditions were found to be initially H₂ and B₅H₁₁, with smaller amounts of B₂H₆, B₆H₁₂, and B₁₀H₁₄ each after an induction period, (see Figs. 1 and 2). There was no evidence for significant amounts of B₅H₉ or B₆H₁₀. From log-log plots of the initial rate of B₄H₁₀ consumption, as well as those for the production of B₅H₁₁ and H₂, it is clear that the initial reaction follows first-order kinetics. Derived activation energies for the three sets of data were E_A(B₄H₁₀) = 99.2±0.8, E_A(B₅H₁₁) = 98.8±1.8, and E_A(H₂) = 107.5±1.9 kJ mol⁻¹, the value from the H₂-data again being slightly higher (as was the case for B₂H₆ in the previous section). The pre-

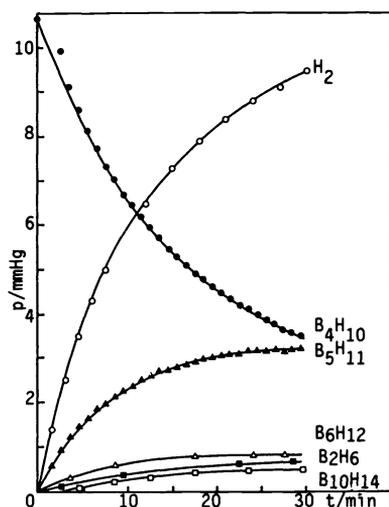


Fig. 1. Reaction profile for thermolysis of B₄H₁₀ at 10.7 mmHg and 78 °C

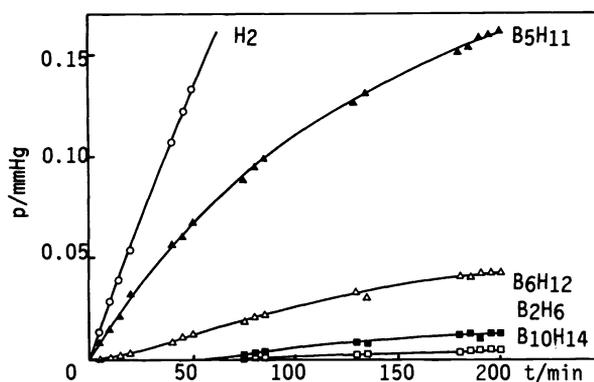
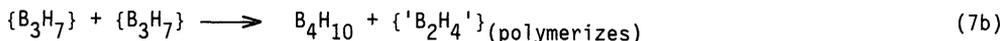


Fig. 2. Reaction profile at high spectrometer gain showing build-up of the volatile boranes during the initial stages of thermolysis of B₄H₁₀ at 3.9 mmHg and 40.2 °C

exponential factor for the first-order disappearance of B₄H₁₀ was $A \approx 6 \times 10^{11} \text{ s}^{-1}$. These results are plotted in Fig. 3 together with earlier data from Schaeffer's group on the cothermolyses of B₄H₁₀ with B₂H₆ and CO (refs. 2a,e). The fact that all the data fall on a single line (upper trace) thus confirms and extends this earlier work and leaves little doubt that the same rate-controlling step (5a) is involved in all three reactions. First-order kinetics would be preserved if this 'slow' step (5a) were followed rapidly by (6) and perhaps (7a) (ref. 25) though the alternative (7b) invoked by Sheldon Shore and his coworkers in a different context (ref. 28) may be preferable (see later).



In addition to the initial homogeneous gas-phase decomposition of B₄H₁₀ to H₂ and B₅H₁₁ (equations 5a and 6) and the formation of solid 'polymer', other boranes (first B₆H₁₂ then B₂H₆ and B₁₀H₁₄) are formed after various periods of induction (Fig. 2 above). Others (refs. 5 and 29) have suggested that B₆H₁₂ might result from the interaction of two {B₃H₇} fragments but in the present system the observed induction period suggests that it is more likely to arise from a cothermolysis reaction involving B₅H₁₁. Likewise, the virtual absence of B₂H₆ in the early stages of the reaction is very significant because it suggests (ref. 25) that a number of steps that have been proposed in the past do not occur in this system. Thus, it is clear that, under these conditions, {B₃H₇} [formed in reaction (6)] does not react with B₄H₁₀ to give B₅H₁₁ and B₂H₆, or with {B₄H₈} to give B₅H₉ and B₂H₆, or with itself to give {B₄H₈} and B₂H₆, though all these reactions have previously been proposed (ref. 5). Likewise, the self-reaction of 2{B₄H₈} to form either B₆H₁₀ and B₂H₆ or B₅H₉ and {B₃H₇} are also ruled out on this basis, and their reaction to form, B₅H₁₁ and 'B₃H₅(polymer)', for which there is good evidence in a different context (ref. 28) is unlikely to be an important route in the presence of a vastly greater concentration of B₄H₁₀.

One further consequence of the recognition of reaction (5a) as the rate-determining step in the thermolysis of B₄H₁₀ is the corollary that an excess of H₂ should inhibit the decomposition of B₄H₁₀ and increase proportionately its conversion to B₅H₁₁ and B₂H₆ [via reaction (6) and the reverse of reactions (1)-(3)] at the expense of the formation of involatile solids. Indeed, there are qualitative observations to this effect in the early literature (refs. 22, 30). We wished to put these observations on a more quantitative basis and accordingly, we thermolysed a mixture of B₄H₁₀ (3.5 mmHg) and H₂ (20 mmHg) at temperatures in the range 50-110 °C. The results are included in Fig. 3 (lower line) from which it is apparent that the activation energy remains unaltered though the absolute rate of the decomposition has diminished by a factor of ~5 (ref. 21). These observations provide cogent additional evidence that B₄H₁₀ decomposes *via* the single rate-determining initial step (5a) since, if (5b) also occurred, suppression of (5a) would inevitably alter the observed activation energy towards that of (5b) which is most unlikely to be fortuitously identical to that of (5a).

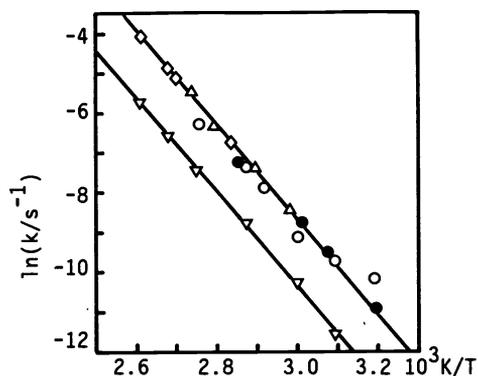


Fig. 3. Arrhenius plot for thermolysis of B₄H₁₀ alone ●, with CO ◊ (ref. 2e) with B₂H₆ △ (ref. 2a) and with B₆H₁₀ ○. The lower set of points ▽ refers to thermolysis of B₄H₁₀ in the presence of an excess of H₂

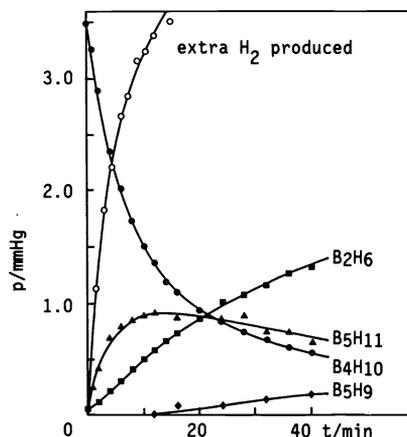


Fig. 4. Reaction profile for the cothermolysis of a mixture of B₄H₁₀ (3.5 mmHg) and H₂ (20 mmHg) at 100 °C; the curve for H₂ represents the extra H₂ generated during the reaction

The detailed product analysis of this cothermolysis of (B₄H₁₀ + 6H₂) is illustrated by the typical reaction profile in Fig. 4: the relative rates of B₅H₁₁ production to B₄H₁₀ consumption are unaltered from those of the thermolysis of B₄H₁₀ alone, whereas there is a marked increase in the relative rate of production of B₂H₆ and almost complete inhibition of 'polymer' formation. The most striking effect is the complete absence of volatile higher boranes such as B₆H₁₂ and B₁₀H₁₄.

All the effects of added H₂ can be interpreted on the basis of reactions already discussed. The inhibition is brought about by the increased importance of the back-reaction (-5a) which is in competition with the production of B₅H₁₁ via reaction (6). The relative increase in the rate of production of B₂H₆ undoubtedly stems from the removal of the {B₃H₇}, concurrently formed in step (6), via (-3) and (-2) in conjunction with (-1). The rapid removal of {B₃H₇} likewise explains both the inhibition of polymer formation via reaction (7a) and/or (7b), and also the inhibition of B₆H₁₂ formation, which probably arises in the normal thermolysis via reactions (8) and/or (9):



For reasons already outlined the alternative suggested route to B₆H₁₂ (namely 2{B₃H₇} → B₆H₁₂ + H₂) seems less likely though this would also be suppressed by added H₂.

THERMOLYSIS OF B₅H₁₁ ALONE AND WITH ADDED H₂

Although there have been several reports in the past of qualitative studies dealing with the thermolysis of B₅H₁₁ (refs. 15b, 19, 30, 31), not all of which agree about the details, there has been no attempt to establish the kinetics of this reaction. Our own work is still in progress (ref. 21) but we can report some of the main findings and their implications.

The thermolysis of pure B₅H₁₁ at pressures of 1.8-10.4 mmHg and temperatures in the range 60-150 °C is found to be first-order in B₅H₁₁ with an activation energy of 73.2±3.7 kJ mol⁻¹ and a pre-exponential factor of 1.65×10⁷ s⁻¹. The main volatile products are H₂ and B₂H₆, and these appear at rates of approximately 1 and 0.5 mole per mole of B₅H₁₁ consumed. A small 'steady-state' concentration of B₄H₁₀ is also present but, in agreement with the earlier work of Burg and Schlesinger (ref. 30), B₅H₉ is not detected in the initial stages. Others have claimed that B₅H₉ is formed from the outset (refs. 15b and 19) but we find that it builds up rather slowly as the reaction proceeds. B₁₀H₁₄ is also produced in low concentration, but as much as 50% of the boron ends up as solid 'polymer'.

The initial step in the decomposition is generally held to be the reversible dissociation (10),



and our own observations are entirely consistent with this being the rate-determining step. The initial rate of production of B₂H₆ is then readily explained by its formation from {BH₃}

via reaction (-1) in ca. 100% yield. The fate of the {B₄H₈} produced in reaction (10) is less obvious. Long has conjectured (ref. 5) that it may react with itself to produce {B₃H₇} and B₅H₉, and subsequently with the {B₃H₇} to produce B₂H₆ and more B₅H₉. This would account for the B₅H₉, but would not explain its absence in the early stages. Moreover, there is as yet no direct evidence for such reactions, and in the preceding section we argued against their involvement in the B₄H₁₀ thermolysis, in which {B₄H₈} features prominently. Lipscomb has calculated that the reaction of {B₄H₈} with B₅H₁₁ to give B₄H₁₀ is exothermic by 125.5 kJ mol⁻¹, and has suggested that this may be an important route to B₅H₉ (ref 4c). As Lipscomb has pointed out, at the temperatures required to decompose B₅H₁₁, B₄H₁₀ would be decomposed to {B₄H₈} and H₂, so that {B₄H₈} is essentially a catalyst for the loss of H₂ from B₅H₁₁ in this reaction. Whilst this reaction may contribute to the production of B₅H₉ and B₄H₁₀ in this thermolysis, it is clear from the evidence that it is not a major sink for the {B₄H₈} produced in reaction (10). An alternative possibility is that {B₄H₈} and B₅H₁₁ react to form n-B₉H₁₅ via reaction (11). An advantage of this step is that it would nicely explain the



observed very high initial production of H₂. The n-B₉H₁₅ is presumed to be unstable under the prevailing conditions, decomposing via B₈H₁₂ (see later) to produce 'polymer' and B₁₀H₁₄. Reaction (11) was used by Long (ref. 5) to explain the observation (ref. 32) that n-B₉H₁₅ is the main product when B₅H₁₁ and B₂H₆ are held together under pressure at room temperature for a few days. The B₂H₆ in this reaction was regarded as playing the dual role of increasing the {B₄H₈} concentration by syphoning off the {BH₃} molecules formed in (10), and stabilizing the n-B₉H₁₅ via the reversible reaction with B₈H₁₂ (ref. 5). We intend to test the possibility that reaction (11) is operative, by thermolysing B₅H₁₁ under hot/cold conditions in an attempt to stabilize the n-B₉H₁₅ as it is formed.

It is of interest to compare the Arrhenius parameters for B₅H₁₁ with those for B₄H₁₀, and to consider the wider implications of the results. The value of 6x10¹¹ s⁻¹ recorded above for the pre-exponential factor for B₄H₁₀ is reasonable for a unimolecular reaction (ref. 33) and is consistent with the proposed mechanism in which H₂ is ejected via a loosely bound transition state. The value for B₅H₁₁ is lower by more than 4 orders of magnitude (1.6x10⁷ s⁻¹) and this implies considerable re-organization to a tightly bound transition state. This is consistent with the more dramatic structural changes which accompany the release of a BH₃ group from the cluster, and it will be of interest to see whether this behaviour is mirrored in the B₆H₁₂ thermolysis, which we are also currently investigating. The considerably greater activation energy for B₄H₁₀ compared with that for B₅H₁₁ reflects a more dramatic temperature dependence of the rate constant for the former, and, from the initial rate laws, the ratio k_{B₄H₁₀}/k_{B₅H₁₁} is found to vary from ~48.9 at 200 °C to ~1.67 at 40 °C. In consequence, at the lower temperatures, the rate of decomposition of the B₅H₁₁ produced in the thermolysis of B₄H₁₀ is only slightly less than the rate of decomposition of B₄H₁₀ itself. There is therefore a need for caution in interpreting the initial-rate data in terms of possible stoichiometries for the reaction. In the light of this new information it may seem surprising that B₅H₁₁ builds up to the extent that it does in the B₄H₁₀ thermolysis, but it must be remembered that both {B₄H₈} and {BH₃}, the initial products of the decomposition of B₅H₁₁ [see reaction (10)], themselves react further with B₄H₁₀ to regenerate B₅H₁₁ [reactions (6) and (-12)].

It has often been suggested (refs. 2a, 22, 30) that B₅H₁₁ and B₄H₁₀ are interconvertible in the presence of H₂, according to the 'equilibrium' (12). However, it was not clear whether



the forward reaction (12) occurred as a single step (i.e. BH abstraction by H₂ from B₅H₁₁ to give {BH₃}) or as a combination of reactions (10) and (-5a). We have now established unequivocally that the latter is the case, by studying the thermolysis of B₅H₁₁ in the presence of added H₂ over a wide range of temperature (ref. 21). The rate of thermolysis was found to be largely unaffected by the presence of an excess of H₂ (see Fig. 5), suggesting that the rate-determining step remains the same, i.e. reaction (10).

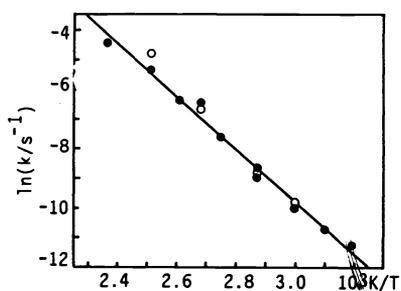


Fig. 5. Arrhenius plot for thermolysis of B₅H₁₁ at a pressure of 3.5 mmHg alone ●, and with 50 mmHg added H₂ ○

THERMOLYSIS AND COTHERMOLYSIS REACTIONS OF B₆H₁₀

A particularly intriguing aspect of the thermolysis of B₂H₆ is the virtual absence of hexaboranes and other species intermediate between the pentaboranes and B₁₀H₁₄. Schaeffer has suggested (ref. 2j) that B₆H₁₀ may play a crucial role by virtue of its known tendency (albeit under somewhat different conditions) to react as a Lewis-base (refs. 34,35) with a Lewis-acid borane intermediates such as {BH₃}, {B₃H₇}, {B₄H₈}, B₈H₁₂, and {B₉H₁₃} to produce larger boranes such as B₁₃H₁₉, B₁₄H₂₂, and B₁₅H₂₃. Just how important this role is will depend on the extent to which B₆H₁₀ is actually produced in the B₂H₆ decomposition, and at present this is simply not known. Under certain conditions {BH₃} can react with B₅H₉ to produce a hexaborane (ref. 3d), though this was not specifically identified as B₆H₁₀, and Long (ref. 5) has proposed several possible routes involving the reactive intermediates {B₃H₇} and {B₄H₈} e.g. {B₃H₇} + B₅H₉ → B₂H₆ + B₆H₁₀, 2{B₄H₈} → B₂H₆ + B₆H₁₀, and {B₄H₈} + B₅H₉ → {B₃H₇} + B₆H₁₀. It is also established that B₈H₁₂ decomposes via the first-order reaction (13) to give B₆H₁₀ and solid polymer (ref. 2g). We are at present



devising ways of testing some of these steps experimentally, but in the meantime, to establish the likely behaviour of B₆H₁₀ under gas-phase thermolytic conditions, we have carried out systematic studies of its thermolysis, both alone, and in the presence of other species.

The gas-phase thermolysis of B₆H₁₀ for pressures in the range 1-7 mmHg and temperatures between 75 and 165 °C was found, perhaps surprisingly, to proceed by a second-order process, with an activation energy of 79.7 ± 2.7 kJ mol⁻¹ and a pre-exponential factor of 4.7 × 10⁶ m³ mol⁻¹ s⁻¹ (ref. 14). In the initial stages a typical reaction produces 1 mole of H₂ per mole of B₆H₁₀ consumed, and deposits some 90% of the reacted borane from the gas phase as a yellowish non-volatile solid hydride of approximate composition BH_{1.33}, which then loses more H₂ to give an insoluble, intractable solid of composition BH_x (where x is ~1.0). Minor amounts of B₅H₉ and B₁₀H₁₄ in an approximate molar ratio of 5:1 are also produced. B₂H₆, B₈H₁₂, B₉H₁₅, as well as B₁₃, B₁₄, and B₁₅ species are detected only in trace amounts at various stages of the reaction and do not accumulate in the gas phase. Added hydrogen has no observable effect on the course of the reaction

On the basis of these results it seemed likely that there were at least two reaction pathways involved in the thermolysis: a major route leading to the non-volatile solid and H₂, and a minor route producing B₅H₉ and B₁₀H₁₄. In the absence of evidence to the contrary, there seemed little justification for considering mechanisms more complex than ones involving a rate-controlling bimolecular interaction between two molecules of B₆H₁₀, and the main task was to deduce the fate of the activated complex {B₁₂H₂₀}[‡]. Such a scheme was devised (ref. 14) leading to an overall stoichiometry for this minor route of 5B₆H₁₀ → 4B₅H₉ + B₁₀H₁₄. Notwithstanding the good agreement between the predicted B₅H₉:B₁₀H₁₄ ratio and that observed experimentally, it seemed unlikely that the situation would be as simple as outlined. Accordingly, further experiments were undertaken (ref. 36) including thermolysis in the presence of CO (to be reported elsewhere) and thermolytic experiments leading to the isolation of a new borane B₂₄H₃₀, which appears to be the conjuncto dimer of the recently identified molecule B₁₂H₁₆ (ref. 37).

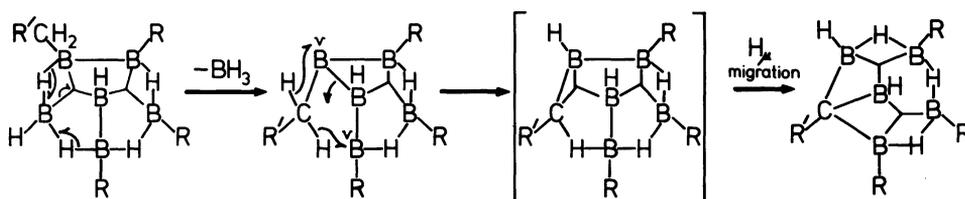
Surface studies (ref. 36)

To check for a possible heterogeneous component in the reaction rates, a thermolysis of B₆H₁₀ was carried out at 3.5 mmHg and 153 °C in a clean 1 l pyrex bulb packed with Raschig rings so as to increase the surface-to-volume ratio by a factor of 33. The effect was dramatic, and unexpected: the rate of decomposition decreased by an order of magnitude relative to the rate in a conditioned unpacked vessel. In successive runs the rate slowly recovered, presumably as the surface of the vessel became deactivated with a coating of the solid product. This behaviour is typical of radical chain reactions (ref. 33), the effect of the clean glass surface being to attract the reactive species, thereby preventing further reaction. Consistent with this it was found that treatment of the clean glass surfaces of a packed reaction vessel with a covering of PTFE polymer, (CF₂)_n, scarcely affected the rate as observed in a packed conditioned vessel. The rate observed in an unpacked PTFE-coated vessel was actually faster than in an unpacked conditioned vessel, suggesting that the coated surface was even less active in removing radicals than was the borane-conditioned surface. Clearly the possibility of a radical-based mechanism for the thermolysis of B₆H₁₀ required careful investigation.

Cothermolysis of B₆H₁₀ with ethene and propene (ref. 36)

Ethene and propene are well known 'radical scavengers' (ref. 33). With B₆H₁₀ these unsaturated hydrocarbons were found to inhibit the reaction dramatically. For a pressure of 3.5 mmHg the decomposition at 165 °C normally has a half-life of ca. 100 min, whereas in the presence of 15 mole % of ethene it is stable over a period of several days. Propene has a more pronounced effect, the addition of only 3% causing complete inhibition in the thermolysis of B₆H₁₀ (3.5 mmHg) for some 20 min. even at 185 °C; larger additions increase the inhibition period proportionately.

The initial products of the cothermolysis, which are very slow to appear at these temperatures because of the limited extent of reaction, are trialkylboranes and the basal-alkylated hexaboranes $B_6H_{10-x}R_x$ ($R = Et$ or Pr , $x = 1-5$), many of which are new compounds. These are followed by the series of alkylated monocarbaboranes $R'CB_5H_8-xR_x$ ($x = 0-3$), where $R' = Me$, $R = Et$ for the ethene reaction, and $R' = Et$, $R = Pr$ for the propene reaction. In one cothermolysis involving propene, which was allowed to go almost to completion, the main products were found to be $B_6H_5Pr_5$ and $EtCB_5H_8-xPr_x$ ($x = 0-3$). It would therefore appear that the alkylboranes $B_6H_{10-x}Pr_x$ ($x = 1-4$) have by this stage of the reaction been converted to the corresponding monocarbaboranes, whereas the end-member of the series, in which all the basal terminal protons have been replaced, possesses enhanced stability. This suggests that the ready formation of the monocarbaborane involves $\{BH_3\}$ release from the base of the corresponding alkylborane, followed by incorporation of the methylene carbon and its associated protons into the ring (Scheme 1).

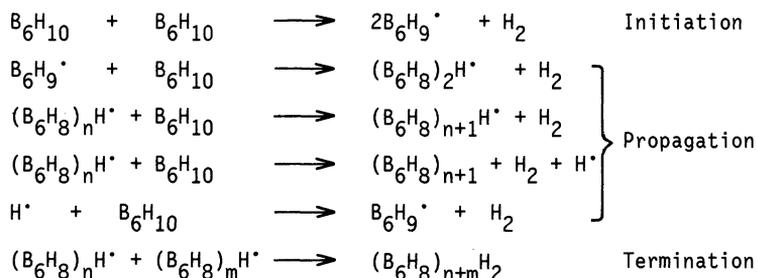


Scheme 1. Possible mechanism for the formation of $R'CB_5H_8-xR_x$ ($x = 0-3$) by elimination of $\{BH_3\}$ from $R'CH_2B_6H_9-xR_x$ ($x = 0-3$). ($R = Et$ or H , $R' = Me$; $R = Pr$ or H , $R' = Et$)

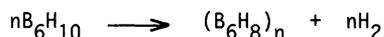
In the case of the penta-alkylated species, $\{BH_3\}$ release is precluded and the formation of the monocarbaborane inhibited. Its virtual absence also indicates that hydroboration of the monocarbaboranes themselves does not occur. In the presence of alkene, $\{BH_3\}$ is readily hydroborated, which accounts (in part) for the appearance of boron trialkyls.

Mechanism of B_6H_{10} thermolysis

In the light of the observed inhibitory effects of active surfaces and unsaturated hydrocarbons, there seems little doubt that the main reaction in the B_6H_{10} decomposition is a radical-type chain process. The reactive species formed in the initiation step is thought to be a genuine (odd-electron) free-radical and not simply a non-soluble reactive borane intermediate analogous to $\{BH_3\}$, $\{B_3H_7\}$, or $\{B_4H_8\}$. In the thermolyses of other boranes, as discussed earlier, such species are undoubtedly present but the reactions are not inhibited in the same dramatic way. There are indications that B_5H_9 (ref. 38) and $B_{10}H_{14}$ (ref. 39) may also decompose via radical intermediates, but detailed evidence is lacking. The initial products of the B_6H_{10} /alkene reactions provide further crucial insights into the mechanism. In particular, the fact that monoalkylated hexaboranes are the very first species to appear (along with boron trialkyls, whose significance is discussed later) provides very strong, if not conclusive, evidence that the radical intermediate formed in the initiation step is in fact $B_6H_9^{\cdot}$. In the absence of 'trapping' agents, this species will react further with B_6H_{10} , setting in train a series of events leading to the removal of some 90% of the boron from the gas phase as non-volatile oligomers. The overall mechanism, though undoubtedly complex, must resemble very closely the classic mechanism proposed for free-radical polymerization of olefins (ref. 33). This features addition of the monomer to the growing radical chain, thereby increasing its length without altering the ability of the radical to react. A possible mechanism for the thermolysis of B_6H_{10} is thus:



When n is large the overall stoichiometry is seen to be



To account for the observed second-order kinetics (ref. 14) it is necessary to include a bimolecular initiation step involving interaction between two B_6H_{10} molecules to produce the $B_6H_9^{\cdot}$ radical. The termination steps involve any two radicals, including identical ones. The scheme provides a general description of the kinetic behaviour of the system under

thermolytic conditions, and satisfactorily explains the overall initial stoichiometry. As the reaction proceeds, further crosslinking undoubtedly occurs, with consequent evolution of additional hydrogen. The scheme as written does not account for the appearance of specific species such as B₁₃H₁₉, B₁₄H_x, B₁₅H₂₃ etc., but this could be dealt with by including the possibility of disproportionation in the termination steps. Such species are observed in only trace amounts in the gas phase, but are the major non-volatile products of 'hot/cold' reactions of B₆H₁₀.

The observation that the alkylhexaborane-carbaborane conversion can occur readily only when {BH₃}-release is possible, inevitably raises the question as to whether B₆H₁₀ itself can release {BH₃} in this way, i.e. via reaction (14). In fact there is good evidence that this



may well be the route to the minor products of the B₆H₁₀ thermolysis, rather than the bimolecular step suggested earlier. Further work will be necessary to establish whether this side-reaction is (as we would now predict) a first-order reaction, but the observed products are certainly consistent with the existence of reaction (14). Both B₅H₉ and B₁₀H₁₄ could arise from the reactive intermediate {B₅H₇}, the former via its reaction with the H₂ produced in the main reaction, and the latter via its self-association. The {BH₃} produced in reaction (14) would probably form B₂H₆, which in cothermolysis with B₆H₁₀ would immediately give B₁₀H₁₄ (see later). In the cothermolysis of B₆H₁₀ and alkenes, in which the main reaction to give solids is inhibited, boron trialkyls are produced in much greater concentration and at an earlier stage than the monocarbaboranes. It is therefore suggested that they arise not only from hydroboration of the {BH₃} eliminated in the conversion of the alkylated hexaboranes to the monocarbaboranes, but also from that produced in reaction (14).

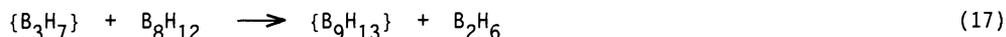
Cothermolysis of B₆H₁₀ with other boranes (ref. 21)

Having established the nature of the B₆H₁₀ self-thermolysis, preliminary cothermolysis reactions were attempted with B₂H₆, B₄H₁₀, B₅H₉, and B₅H₁₁. In all cases except B₅H₉, the rate of consumption of B₆H₁₀ was found to be more rapid than in the self-thermolysis, clearly indicating that interactions were occurring. Detailed kinetic studies with B₂H₆ and B₄H₁₀ showed that in each case the rate was governed by the rate-determining sequence of the co-reactant. Thus with B₂H₆ the reaction was found to be 3/2-order in B₂H₆ and zero order in B₆H₁₀, whereas with B₄H₁₀ the reaction was first-order in B₄H₁₀ and zero-order in B₆H₁₀. The rate data for disappearance of B₂H₆ and B₄H₁₀ (see Fig. 3) when cothermolysed with B₆H₁₀ are compatible with the Arrhenius plots for the self-reactions of these boranes. Thus, the activation energy, E_A, for cothermolysis of B₆H₁₀/B₂H₆ is 98.8±3.9 kJ mol⁻¹ compared with 92.3±6.6 kJ mol⁻¹ for thermolysis of B₂H₆ alone, and E_A for B₆H₁₀/B₄H₁₀ is 88.4±6.1 kJ mol⁻¹ compared with 99.2±0.8 kJ mol⁻¹ for B₄H₁₀ alone.

In the B₆H₁₀/B₂H₆ cothermolysis the main volatile product apart from H₂ was found to be B₁₀H₁₄ in yields of up to 40%. Despite the fact that the B₂H₆ decomposition was rate-controlling, very little pentaborane was formed. In the light of these results it is clear that, under the prevailing conditions (100-198 °C), there is no interaction between B₆H₁₀ and either B₂H₆ itself or {BH₃}. Instead it seems likely that B₆H₁₀ reacts with {B₃H₇}, the product of the rate-determining step (3), to give B₉H₁₅ via reaction (15). This step has



been proposed in the past, without direct evidence (ref. 5), and it has been shown that B₆H₁₀ reacts with 10B₃H₇.THF at 0 °C in the presence of BF₃ to give B₉H₁₅ labelled at the 3, 4, and 9 positions (ref. 35b). If B₉H₁₅ is formed, it must then decompose immediately to B₁₀H₁₄. This reaction is known to occur, but isotope studies have shown that it does not take place in a single step (ref. 2g). Thus, in the reaction between B₉H₁₅ and 10B₂H₆, the resulting B₁₀H₁₄ has two labelled boron atoms, implying that the route is via B₈H₁₂. The simplest proposed (ref. 5) sequence of events, reactions (16)-(18), differs from that suggested originally (ref. 35b). So far, it has been assumed that B₆H₁₀ reacts via reaction (15).



It is possible that the B₂H₆ decomposition proceeds as far as the production of {B₄H₈} [reactions (4) and (5a)] before the interaction with B₆H₁₀ occurs to give B₁₀H₁₄, but results discussed later suggest that this is not the case.

In the B₆H₁₀/B₄H₁₀ cothermolysis, B₉H₁₅ is actually observed as a major product in the early stages of the reaction, because the temperatures required for this system are much lower than those necessary to achieve reaction between B₂H₆ and B₆H₁₀. A similar result has been

obtained in the reaction at much lower temperatures between B₄H₈CO and B₆H₁₀ (ref. 35b), and it seems reasonable to invoke reaction (19) in each case. In this respect it is clear that



the previously proposed (ref. 5) reaction of these two species to give 2B₅H₉ is not significant under these conditions.

The results obtained from these two detailed cothermolysis studies demonstrate in a very striking way the strong affinity which exists between B₆H₁₀ and the reaction intermediates {B₃H₇} and {B₄H₈}. In the B₆H₁₀/B₂H₆ cothermolysis, B₆H₁₀ is in competition with B₂H₆ for the {B₃H₇} [reactions (4) and (15)], whereas in the B₆H₁₀/B₄H₁₀ cothermolysis, it competes successfully with B₄H₁₀ for {B₄H₈} [reactions (6) and (19)]. To test these competitive effects further, the effect of adding an excess of H₂ to the two cothermolysis systems has been studied in some detail. The orders of the two reactions were shown to be unaffected by the presence of added H₂, confirming that the respective rate-determining sequences were unaltered, but retardation was observed only in the B₆H₁₀-B₄H₁₀ case. In view of the fact that both the B₂H₆ and B₄H₁₀ self-reactions are retarded by the presence of added H₂ [presumably via reactions (-3) and (-5a), respectively], the lack of inhibition in the B₆H₁₀/B₂H₆/H₂ system, even in the presence of a 10-fold excess of added H₂, demonstrates that B₆H₁₀ is particularly effective in its competition for {B₃H₇}. Returning to an earlier point, it is now clear that B₆H₁₀ does in fact react, in the B₆H₁₀/B₂H₆ cothermolysis, at the {B₃H₇} stage.

PHOTOLYSIS OF BORANES

In comparison with the extensive studies on the thermolysis of boranes, little effort has been directed towards their photolysis, and only in the case of B₂H₆ has there previously been any kinetic treatment of the data. The situation as it existed in 1979 has been reviewed (ref. 40) and there have been relatively few developments since then. Notable among these have been Irion and Kompa's UV-laser photochemical studies at 193.3 nm (ref. 41): from results on the B₂H₆/D₂ exchange reaction and from measurements of the quantum yield of BH₃ [$\phi(BH_3) = 2.0 \pm 0.25$] it was concluded that the primary photochemical step is the same as that proposed in thermolysis: B₂H₆ + hν → 2{BH₃}. As examples of the use of photolysis in borane synthesis we may note the work of Larry Sneddon's group in using mercury photosensitized reactions to make coupled boranes and carbaboranes (ref. 42) and our own work in synthesizing various geometrical isomers of *conjuncto*-icosaborane(26) (ref. 43). Recent work involving the cophotolysis of binary boranes such as B₅H₉ with other gas-phase species such as hexafluoroacetone suggests that there is also great synthetic potential in this area (ref. 44).

Information in the literature on the UV spectra of the binary boranes in the gas phase is surprisingly sparse: only B₂H₆, B₄H₁₀, and B₅H₉ have been studied (refs. 40a, 41a, 45, 46) and they all exhibit weak, featureless absorptions which begin at about 220-230 nm and increase down to the experimentally imposed cut-off at about 185 nm. As a necessary preliminary to a quantitative study of the photolysis of the boranes we have therefore recorded the spectra of a suite of volatile boranes (including those already mentioned and for which agreement with the published data was good). The spectra are illustrated in Fig. 6 and extinction coefficients are summarized in Table 2.

Photolysis studies were carried out in a 1l bulb containing an appropriate Hg lamp (eg. 125 watt medium-pressure, emitting mainly near 365 nm but with smaller amounts at 254, 265, 297, 303, 313, and 334 nm as well). The changing composition of the gas-phase mixture was monitored continuously by mass spectrometry. Non-volatile solids were produced in all the reactions but, with repeated cleaning of the lamp-housing, comparative rate data for the various boranes could be obtained. In kinetic runs various devices were used to calibrate the changing intensity of the transmitted light.

TABLE 2. UV parameters for binary boranes (ref. 36)

Borane	B ₂ H ₆	B ₄ H ₁₀	B ₅ H ₉	B ₅ H ₁₁	B ₆ H ₁₀	B ₆ H ₁₂	n-B ₉ H ₁₅	B ₁₀ H ₁₄
λ_{\max}/nm	<195	<195	<195	209	247	263	260	272
$\epsilon/m^2 \text{ mol}^{-1}$	2.0 ^a	0.71 ^a	88 ^a	82.9	165.1	278.9	~200 ^b	248.6 ^c

^aData refer to ϵ at 195 nm; λ_{\max} is at shorter wavelengths

^bApprox. value: sample decomposed during measurement

^cIn hexane solution

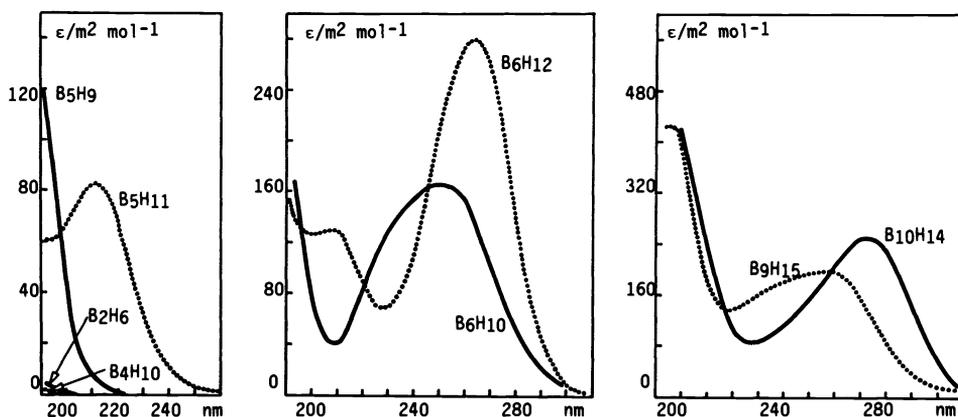


Fig. 6. UV absorption spectra of gaseous boranes ($B_{10}H_{14}$ in hexane solution)

In a series of photolyses B_2H_6 , B_4H_{10} , and B_5H_9 were found to be much more stable than B_5H_{11} , B_6H_{10} , and B_6H_{12} (ref. 36). For example, the initial rates of consumption of the boranes (in arbitrary units) were ~ 0 , 0.33, 2.5, 50, 100, and 380 respectively, and the initial rates of production of H_2 (the main volatile product) were 0.28, 0.20, 0.38, 20, 44, and 400. Qualitative correlation with the absorption spectra in Fig. 6 is clear. Inclusion of Hg vapour in the system increased the rate of B_2H_6 -decomposition about 30-fold but had little effect on the rates of decomposition of the other boranes. Thus, the photolytic stability decreases in the sequence $B_2H_6 > B_4H_{10} \sim B_5H_9 > B_5H_{11} > B_6H_{10} > B_6H_{12}$, in sharp contrast with the thermolytic stability of these boranes which follows the sequence $B_5H_9 > B_2H_6 \sim B_6H_{10} > B_6H_{12} > B_5H_{11} > B_4H_{10}$. The most notable differences are for B_4H_{10} (which is very stable to photolysis but very unstable thermally) and B_6H_{10} , for which the reverse applies. It is also noteworthy that the sequence of photolytic stability for the arachno series ($B_4H_{10} > B_5H_{11} > B_6H_{12}$) is precisely the opposite to that found in thermolysis.

We are at present undertaking a detailed study of the products of photolysis (and cophotolysis) as a function of time in order to establish the mechanistic pathways adopted (ref. 36). Preliminary results indicate that the initial step for B_6H_{12} might well be the elimination of $\{BH_3\}$ to give B_5H_9 and $\{BH_3\}$ as the main product boranes:



Photolysis of B_5H_{11} may also involve facile elimination of $\{BH_3\}$ as the initial step.

A kinetic study of the photolysis of B_6H_{10} has revealed significant differences from the thermolysis studies described in the preceding section. It is well known that radical chain reactions can be initiated either thermally or photolytically, and that the observed kinetics will depend on the mechanism of initiation (ref. 33). The second-order kinetics observed in the thermolysis of B_6H_{10} were interpreted in terms of a bimolecular initiation. Under photolytic conditions at 0 °C, however, first-order kinetics are observed for both consumption of B_6H_{10} and production of H_2 . As in thermolysis the main volatile product was H_2 and most of the boron disappeared from the gas phase. However, a significant difference from thermolysis was that B_2H_6 appeared as the sole volatile borane and B_5H_9 was virtually absent. There was also substantially less H_2 produced proportionately in photolysis, the observed ratio of H_2 produced per mole of B_6H_{10} consumed being closer to 0.5 than the value of 1.0 observed in the initial stages of thermolysis. Further experimental results are required, however, before detailed mechanistic conclusions can be drawn.

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