R+D 5004-CH-01

(2)

A. (1) Kinetics of Boron Hydride Interconversion Reactions

(2) Principal Investigator: Professor N.N. Greenwood

(3) Contractor: University of Leeds,
Attn. The Registrar,
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United Kingdom

(4) Contract Number: DAJA45-86-C-0019

(5) 1st Periodic Report Thru 5th Periodic rpt.

(6) May 1986 ~~- October 1986~~ May 1988

(7) The Research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. ~~This report is intended only for the internal management use of the Contractor and the U.S. Government.~~

B. (1) Scientific work carried out during the reporting period

Hexaborane(12) has been prepared and purified with a view to carrying out detailed kinetic studies of its gas-phase thermolysis. By way of further characterizing this little-studied borane we have taken the opportunity of determining its full n.m.r. parameters, including ^{11}B-^{11}B COSY, ^{1}H-^{1}H COSY, and temperature dependent properties. Electron diffraction experiments have also been initiated in collaboration with Dr D.W.H. Rankin (Edinburgh University) to get detailed geometrical dimensions of B_6H_{12}. Some preliminary work on its chemistry, initiated before the Grant period, has been continued.

The synthesis is in progress of $NaBH_4$, isotopically enriched in ^{10}B, for use as an intermediate in the preparation of specifically labelled boranes. These will be used later in the Project in carefully designed mechanistic experiments.

(2) Future Research Plans

Work will continue along the lines indicated in the Research proposal. In the immediate future it is intended to carry out a detailed kinetic study of thermolysis and cothermlysis reactions of pentaborane(11) over a range of temperature and pressure.

(3) Personnel

Mary Millikan was appointed as a vacation worker to prepare and purify B_6H_{12} and to study aspects of its chemistry. Susan Lucas has been appointed under the terms of the contract as a graduate student to work full-time on the Project. She graduated B.Sc. (Hons.) from the University of Leeds in June 1986 and is registered in the Department of Inorganic and Structural Chemistry as a student doing research for a higher degree.

Associate Investigator

Principal Investigator

30th October 1986

A. (1) Kinetics of Boron Hydride Interconversion Reactions

(2) Principal Investigator: Professor N.N. Greenwood

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(4) Contract Number: DAJA45-86-C-0019

(5) 2nd Periodic Report

(6) Period Ending 30th November 1986

(7) The Research reported in this docuement has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. ~~This report is intended only for the internal management use of the Contractor and the U.S. Government.~~

B. (1) Scientific work carried out during the reporting period

In collaboration with Dr D.W.H. Rankin (Edinburgh University), electron diffraction measurements on hexaborane(12) have now been completed, and the results are being analyzed with a view to determining the detailed molecular structure of this compound in the gas phase.

Several grams of $NaBH_4$, isotopically enriched in ^{10}B have been synthesized, and half of it has been converted to the correspondingly labelled $^{10}B_2H_6$ for subsequent use in the Project in mechanistic studies.

Detailed kinetic studies are now in progress of the thermolysis of pentaborane(11) as a function of temperature and initial pressure. Cothermolysis reactions of this borane with hydrogen and other boranes are also being carried out to gain further insight into certain aspects of the proposed mechanism by which diborane is converted ultimately to decaborane(14).

Following on from our earlier work on hexaborane(10) [1], cothermolysis reactions involving this borane are now being studied in detail. These various measurements are yielding important new information about product analyses, reaction orders, and activation energies, and these will be discussed in more detail in the next Periodic Report when the analysis of data is complete.

(2) Future Research Plans

Work will continue along the lines indicated in the Research proposal.

(3) Personnel

Mary Millikan (vacation worker) is no longer working on the Project. Her appointment came to an end on 24th October 1986. Susan Lucas (graduate student) is continuing to work on the Project. Martin Attwood, a graduate student in the final year of his PhD, has been appointed to work full-time on the Project. He graduated BSc(Hons) from the University of Leeds in June 1984 and is registered as a PhD student in the Department of Inorganic and Structural Chemistry.

References

1. R. Greatrex, N.N. Greenwood, and G.A. Jump, J. Chem. Soc., Dalton Trans., 1985, 541; G.A. Jump, PhD Thesis, University of Leeds, 1984.

Associated Investigator

4th December 1986 Principal Investigator

5004-CH-01.

A.(1) Kinetics of Boron Hydride Interconversion Reactions

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(4) Contract Number: DAJA45-86-C-0019

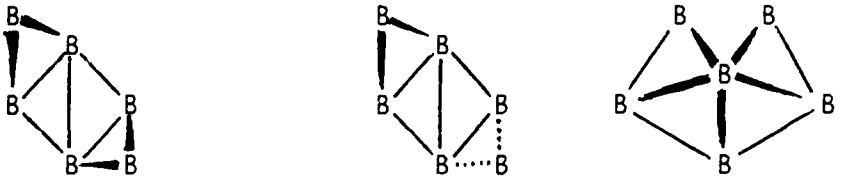
(5) 3rd Periodic Report

(6) Period ending 31st May 1987

(7) The Research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army. ~~This report is intended only for the internal management use of the Contractor and the U.S. Government.~~

B. (1) Scientific work carried out during the reporting period

Preliminary analysis has shown that the electron diffraction data on hexaborane(12) is consistent with a structure having $\underline{C}_2$ symmetry. Alternative arrangements



($\underline{C}_2$) ($\underline{C}_i$) ($\underline{C}_s$)

based on either $\underline{C}_s$ or $\underline{C}_i$ symmetry were also examined, but gave less satisfactory fits to the data. The results are now being refined to give accurate molecular dimensions.

The first ^{10}B-labelled hexaborane(10) has been synthesized. The compound was prepared by the standard method of Shore and co-workers, [1] but enriched $^{10}B_2H_6$ was used in the final stage of the process. On the basis of mass spectrometric and n.m.r. spectroscopic (^{1}H, ^{10}B, ^{11}B) measurements, the single boron label was shown to be located entirely in the base of the pentagonal pyramid. Interestingly, the label was found to scramble into the apex, without associated decomposition, when the sample was heated at 65°C for several hours in toluene. Detailed experiments are planned, with the aim of obtaining rate data and activation energies for this process, in the hope that this information will throw light on the nature of the processes involved in cluster rearrangements.

The thermolysis of pure pentaborane(11) in the gas phase at pressures of 1.8-10.4 mmHg and temperatures in the range 60-150°C has been found to be first-order in B_5H_{11} with an activation energy of 73.2±3.7 kJ mol^{-1} and a pre-exponential factor of 1.65×10^7 s^{-1}. The main volatile products were shown to be H_2 and B_2H_6, and these appeared at rates of approximately 1 and 0.5 mole per mole of B_5H_{11} consumed. A small, steady concentration of B_4H_{10} was present throughout the reaction but, in agreement with the earlier work of Burg and Schlesinger, [2] B_5H_9 was not detected in the initial stages. $B_{10}H_{14}$ is also produced in low concentration, but as much as 50% of the boron is converted to solid 'polymer'. Added hydrogen was found to alter the product distribution in a dramatic way, but the initial rate of decomposition of the B_5H_{11} was unaffected.

Cothermolysis reactions have been carried out between hexaborane(10) and the boranes B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11}. In all cases except B_5H_9, the rate of consumption

of B_6H_{10} was found to be more rapid than in the self-thermolysis, clearly indicating that interactions were occurring. Detailed kinetic studies with B_2H_6 and B_4H_{10} showed that in each case the rate was governed by the rate-determining sequence of the co-reactant.

The kinetic and mechanistic implications of these results are now being assessed, and will be discussed in detail in later Reports.

(2) Future Research Plans

Work will continue along the lines indicated in the Research proposal.

(3) Personnel

Susan Lucas and Martin Attwood are continuing to work on the project as graduate students.

References

1. R.J. Remmel, H.D. Johnson, V.T. Brice, and S.G. Shore, Inorg. Synth., 1979, 19, 247.

2. A.B. Burg and H.J. Schlesinger, J. Am. Chem. Soc., 1933, 55, 4009.

Associate Investigator

Principal Investigator

27th May 1987

A. (1) Kinetics of Boron Hydride Interconversion Reactions

(2) Principal Investigator: Professor N.N. Greenwood

Associate Investigator: Dr R. Greatrex

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(4) Contract Number: DAJA45-86-C-0019

(5) 4th Periodic Report

(6) June 1987 - November 1987

(7) The Research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office of the U.S. Army.

B. (1) Scientific work carried out during the reporting period

(a) The structure of Hexaborane(12).- Arachno-B_6H_{12} is the only simple binary borane for which crystallographic data are not available, the compound forming a glass at low temperature. The electron-diffraction study on this species is now complete, and a paper on the work has been submitted for publication. [1] The gaseous molecule has C_2 symmetry (see Figure 1) with two BH_2 terminal groups, four other terminal hydrogen atoms, and four bridging hydrogen atoms, two of which are asymmetric. The boron framework is a six-atom fragment of the equatorial belt of an icosahedron, and comprises only the second known example of this geometry. The results establish a clear structural relationship between the three arachno- boranes B_4H_{10}, B_5H_{11} (also studied recently with the same equipment [2]), and B_6H_{12}, and this is of relevance to the interpretation of our gas-phase thermolysis results.

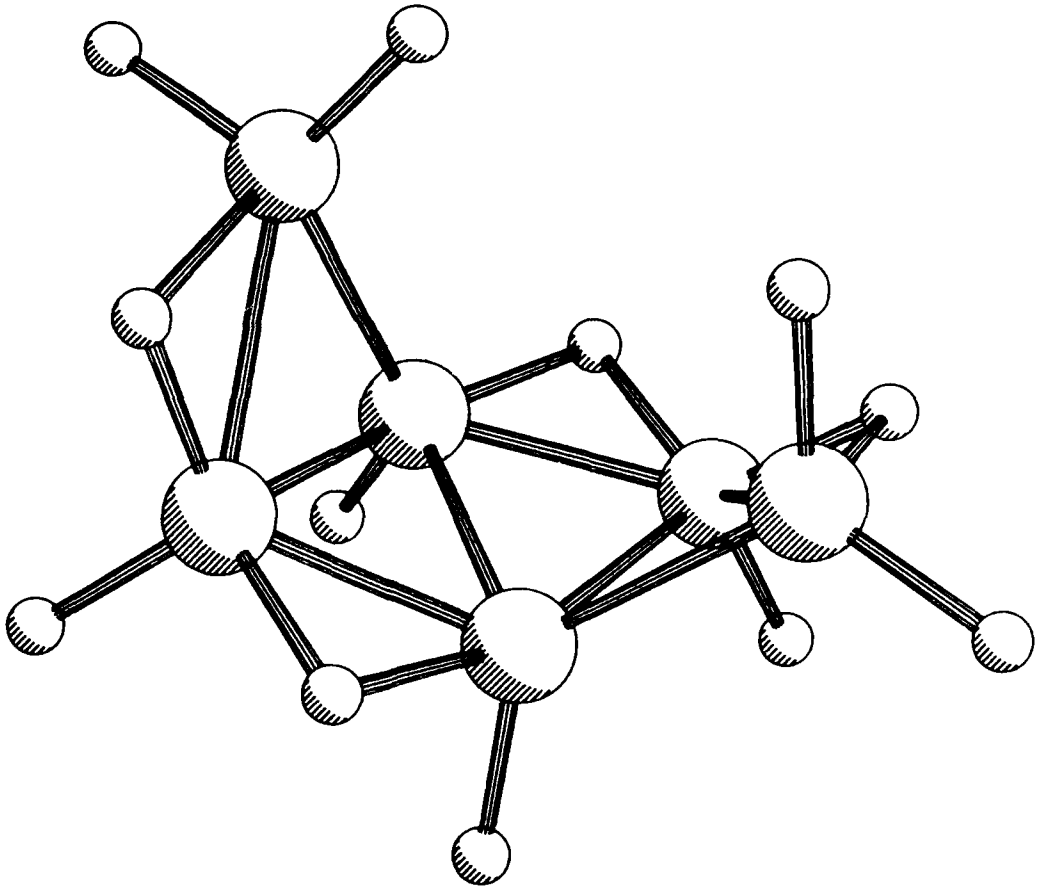

Figure 1. Molecular structure of arachno-B_6H_{12}. [1]

(iii) Autumn Meeting of the Royal Society of Chemistry, University of Nottingham, 22-24 September, 1987. The meeting was atterded by Professor Greenwood and Dr Greatrex. Dr Greatrex gave an invited lecture, [6] and three posters were presented.[7-9]

(iv) Royal Society of Chemistry's Tilden Symposium on Developments in Cluster Chemistry, London, 22 October, 1987. The meeting was attended by Dr Greatrex, Susan Lucas, and Martin Attwood. Dr Greatrex delivered an invited lecture. [10]

(2) Future Research Plans

Work will continue along the lines indicated in the Research proposal.

(3) Personnel

Martin Attwood is no longer working on the project. He has successfully defended his PhD Thesis, [11] and has taken up a postdoctoral appointment with Professor R.N. Grimes in the USA. Susan Lucas has successfully defended her MSc Thesis, [12] and is no longer supported by Grant funds. We hope to recruit a new graduate student in the near future to work on the project.

References

1. R. Greatrex, N.N. Greenwood, M.B. Millikan, D.W.H. Rankin, and H.E. Robertson, "The molecular structure of hexaborane(12) in the gas phase as determined by electron diffraction", J. Chem. Soc., Dalton Trans., submitted for publication.

2. R. Greatrex, N.N. Greenwood, D.W.H. Rankin, and H.E. Robertson, "The molecular structures of pentaborane(9) and pentaborane(11) in the gas phase as determined by electron diffraction", Polyhedron, 1987, 6, 1849.

3. R. Greatrex, N.N. Greenwood, and C.D. Potter, "A Kinetic study of the gas-phase thermolysis of tetraborane(10)", J. Chem. Soc., Dalton Trans., 1986, 81.

4. N.N. Greenwood and R. Greatrex, "Kinetics and mechanism of the thermolysis and photolysis of binary boranes", Pure Appl. Chem., 1987, 59, 857.

5. R. Greatrex, N.N. Greenwood, and S.M. Lucas, "The use of isotopic labels in boron hydride chemistry", paper presented at Intraboron VII, Ross Priory, 16-18 September, 1987.

6. R. Greatrex, "Kinetics and mechanisms of the thermolysis of boron hydrides in the gas phase", Invited Lecture given at the Autumn Meeting of the RSC, Nottingham, 22-24 September, 1987.

7. M.D. Attwood, R. Greatrex, N.N. Greenwood, and C.D. Potter, "The influence of added H_2 on the thermolysis of B_4H_{10}". Poster presented at the Autumn Meeting of the RSC, Nottingham, 22-24 September, 1987.

8. M.D. Attwood, R. Greatrex, and N.N. Greenwood, "Thermolysis of B_5H_{11} alone and with added H_2". Poster presented at the Autumn Meeting of the RSC, Nottingham, 22-24 September, 1987.

9. M.D. Attwood, R. Greatrex, and N.N. Greenwood, "Cothermolysis of B_6H_{10} with other boranes". Poster presented at the Autumn Meeting of the RSC, Nottingham, 22-24 September, 1987.

10. R. Greatrex, "Thermal interconversions of boranes". Invited Lecture at the RSC's Tilden Symposium, London, 22 October, 1987.

11. M.D. Attwood, PhD Thesis, "Gas-phase thermolysis and cothermolysis of boron hydrides". University of Leeds, 1987.

12. S.M. Lucas, MSc Thesis, "The use of isotopic labels in boron hydride chemistry". University of Leeds, 1987.

Associate Investigator

Principal Investigator

24th November 1987

A. (1) Kinetics of Boron Hydride Interconversion Reactions

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(4) Contract Number: DAJA45-86-C-0019

(5) 5th Periodic Report

(6) December 1987 - May 1988

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B. (1) Scientific work carried out during the reporting period

As discussed in B(3) Dr Martin Attwood is no longer working on the project. His PhD Thesis is now available and a copy is enclosed with this Report. [1] Two papers based on the work reported in the Thesis have been submitted for publication, [2,3] Likewise, Miss Susan Lucas, who was supported on the grant, has successfully completed her MSc degree and a copy of her thesis is enclosed. [4] We do not at present have a graduate student working on the project, but the two senior investigators have continued the work with the assistance of our Experimental Officer, Mr Darshan Singh and several other graduate students receiving financial support from the Science and Engineering Research Council. Some areas of work in which progress has been made are now summarized.

(a) Kinetics and mechanism of the thermal decomposition of hexaborane (12) in the gas phase.- [5,6] The first quantitative kinetic study of the gas-phase thermolysis of arachno-B_6H_{12} has been shown to produce predominantly B_5H_9 and B_2H_6 in a molar ratio of 2:1 via a first-order reaction having Arrhenius parameters which are essentially identical to those reported for the decomposition of the structurally-related B_5H_{11}, [1,2] These results imply a mechanism involving BH_3-elimination as the rate-determining initial step in both reactions, followed by the rapid dimerization of this reactive intermediate to give B_2H_6. Thus, in the case of B_6H_{12} the initial steps in the thermolysis are thought to be as follows:

$$B_6H_{12} \longrightarrow B_5H_9 + \{BH_3\} \text{ (slow)} \qquad (1)$$

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

A preliminary report of this work has been accepted for publication, [5] and further work is in progress to determine whether the small amounts of B_6H_{10} produced in this reaction arise from a competing, but minor, reaction channel involving direct elimination of H_2 from B_6H_{12}. [6]

(b) Arachno-B_4H_8CO.- [7] A high-pressure-bomb apparatus has been set up, and used for the successful synthesis of this material from either B_4H_{10} or B_5H_{11} and CO, using methods described in the literature. Several different samples have been studied in collaboration with Dr X.L.R. Fontaine (Leeds University) by ^1H- and ^{11}B-nmr, and shown to contain endo and exo isomers in the approximate ratio 62/38. Moreover, this ratio is independent of temperature, which suggests that the two isomers are formed initially in these particular proportions, and are not involved in a thermal equilibrium.

An electron diffraction study is being carried out on this material in collaboration with Dr D.W.H. Rankin (Edinburgh University), with a view to determining its detailed molecular structure in the gas phase. In addition, a new apparatus has been designed and constructed, to enable the gas-phase thermolysis of this rather unstable compound to be studied over a range of initial pressures and temperatures.

(c) Isotope studies.- [8] Work is continuing in this area and will be discussed in future Reports as appropriate.

(2) Personnel

As discussed in the previous Report, Martin Attwood and Susan Lucas are no longer being supported by Grant funds. Copies of their Theses are now available and are enclosed with this Report. [1,4] The work of the two senior investigators, Professor N.N. Greenwood and Dr R. Greatrex, continues along the lines previously outlined, and we hope to recruit a new graduate student in the near future to work on the project. As indicated earlier in the Report, Mr Darshan Singh and several graduate students with support from the Science and Engineering Research Council have been assisting the two senior investigators with their work on the project.

References

1. M.D. Attwood, PhD Thesis, "Gas-phase thermolysis and cothermolysis of boron hydrides", University of Leeds, 1987.

2. M.D. Attwood, R. Greatrex, and N.N. Greenwood, "A kinetic study of the gas-phase thermolysis of pentaborane(11)", J. Chem. Soc., Dalton Trans., submitted for publication.

3. M.D. Attwood, R. Greatrex, and N.N. Greenwood, "The influence of added hydrogen on the kinetics and mechanism of thermal decomposition of tetraborane(10) and of pentaborane(11) in the gas phase", J. Chem. Soc., Dalton Trans., submitted for publication.

4. S.M. Lucas, MSc Thesis, "The use of isotopic lables in boron hydride chemistry", University of Leeds, 1987.

5. R. Greatrex, N.N. Greenwood, and S.D. Waterworth, "Kinetics and mechanism of the thermal decomposition of hexaborane(12) in the gas phase", J. Chem. Soc., Chem. Commun., 1988, in the press.

6. R. Greatrex, N.N. Greenwood, and S.D. Waterworth, unpublished results, University of Leeds, 1988.

7. S.J. Cranson, P.M. Davies, R. Greatrex, and N.N. Greenwood, unpublished results, University of Leeds, 1988.

8. R. Greatrex, N.N. Greenwood, and S.L. Lucas, unpublished results, University of Leeds, 1988.

Associate Investigator

Principal Investigator

24th May 1988

Pure & Appl. Chem., Vol. 59, No. 7, pp. 857–868, 1987.
Printed in Great Britain.

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 H_2 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 B_2H_6, B_4H_{10}, B_5H_{11}, and B_6H_{10} are discussed, as are the effects of added H_2 and the cothermolysis of B_6H_{10} with alkenes. The final section presents data on the UV absorption spectra and photolytic stability of eight volatile boranes and the reaction kinetics of B_6H_{10} 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 B_2H_6, B_4H_{10}, and B_5H_{11} 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 B_4H_{10} as the first isolable intermediate, followed by B_5H_{11}. 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 $\frac{1}{2}H_2(g)$, 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 C_2H_6 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 BMe_3 (372 kJ mol^{-1}). The value of

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

$\Delta H°f,298$/kJ mol^{-1} (refs.8,9)		$\bar{E}(X-Y)$/kJ mol^{-1} (ref. 9)		$\bar{E}(X-Y)$/kJ mol^{-1} (refs. 8,10)	
H(g)	½x436	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

[a]Value derived for C-Me in C_2H_6; this is slightly lower than the value of 356 kJ mol^{-1}for the heat of atomization of diamond.
[b]Value derived for B-Me in BMe_3; similar values are obtained from BEt_3, BBu_3, and BCy_3, but the values for B-Ph from BPh_3 and Ph_2BCl 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 CH_4) and E(H-H) in H_2. 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 B_2H_6 will be briefly reviewed. This will be followed by more substantial sections on the thermolysis of B_4H_{10}, B_5H_{11} and B_6H_{10} alone, and their cothermolysis with dihydrogen (or deuterium) and other boranes. The cothermolysis of B_6H_{10} 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 B_2H_6 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 ½, 1, 3/2, 2, 5/2, or variable, but there is now general acceptance that, for the homogeneous gas-phase thermolysis of B_2H_6 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 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:

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

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

$$\{B_3H_9\} \xrightarrow{\text{slow}} \{B_3H_7\} + H_2 \quad (3)$$

The dissociation equilibrium (1) generates the reactive intermediate $\{BH_3\}$; this reacts with more B_2H_6 (step 2) to generate $\{B_3H_9\}$ which then loses dihydrogen in the rate-determining step (3). Theoretically-calculated reaction profiles have raised the possibility that the formation of $\{B_3H_9\}$ 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 B_2H_6, the 'observed' rate of (2) is some 10^3-times faster than that of reaction (3) (ref. 3e). There is now also good experimental evidence for the reactive intermediates $\{BH_3\}$ and $\{B_3H_7\}$ 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 H_2, B_5H_{11}, B_5H_9, and $B_{10}H_{14}$ together with smaller amounts of B_4H_{10} and traces of B_6H_{10}, B_6H_{12}, B_8H_{12}, and B_9H_{15}. There was no evidence for heptaboranes or $B_{20}H_{26}$ under these conditions. Reaction orders (determined from initial rates) both for B_2H_6 loss and H_2 production were close to 3/2. From the B_2H_6 data the activation energy E_A was 92.3±6.6 kJ mol^{-1} and the preexponential factor A was 1.58x10^8 m$^{3/2}$ mol$^{-\frac{1}{2}}$ s^{-1}. The correponding Arrhenius parameters from the initial rates of H_2 production were somewhat higher (E_A =113.0±7.3 kJ mol^{-1} and A = 3.08x10^{10} m$^{3/2}$ mol$^{-\frac{1}{2}}$ s^{-1}) possibly because the H_2 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 H_2 is known to inhibit the decomposition of B_2H_6 (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 B_2H_6 at 3.5 mmHg and 150 °C is decreased by a factor of 3.4 in the presence of a 14-fold excess of H_2. Further quantitative work is planned in this area.

THERMOLYSIS OF B_4H_{10} AND ITS EXCHANGE WITH D_2

There is now little doubt that B_4H_{10} is the first isolable species in the thermolysis of B_2H_6 (ref. 2c). It is formed via reaction (4), though under normal thermolytic conditions

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

it is itself too unstable to be readily observed. Its thermolysis, like that of B_2H_6, 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 B_4H_{10} might decompose by two simultaneous unimolecular paths (5a and 5b):

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

$$B_4H_{10} \rightleftharpoons \{B_3H_7\} + \{BH_3\} \qquad (5b)$$

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 B_4H_{10} and D_2 (ref. 26) led to the rejection of (5a) as an acceptable reaction step in the thermolytic decomposition of B_4H_{10} (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 B_4H_{10}:3D_2 undergoes rapid and extensive exchange at 42 °C (a temperature at which the rate of thermal decomposition of B_4H_{10} 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. $\{B_3H_7\} + D_2 \longrightarrow \{B_3H_7D_2\}$, can be ruled out at these temperatures since the subsequent decomposition of the postulated isotopomer of $\{B_3H_9\}$ is the rate-determining step (3) in the decomposition of B_2H_6 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 B_4H_{10}. 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 B_4H_{10} 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 B_4H_{10} 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 B_4H_{10} under these conditions were found to be initially H_2 and B_5H_{11}, with smaller amounts of B_2H_6, B_6H_{12}, and $B_{10}H_{14}$ each after an induction period, (see Figs. 1 and 2). There was no evidence for significant amounts of B_5H_9 or B_6H_{10}. From log-log plots of the initial rate of B_4H_{10} consumption, as well as those for the production of B_5H_{11} and H_2, it is clear that the initial reaction follows first-order kinetics. Derived activation energies for the three sets of data were $E_A(B_4H_{10})$ = 99.2±0.8, $E_A(B_5H_{11})$ = 98.8±1.8, and $E_A(H_2)$ = 107.5±1.9 kJ mol^{-1}, the value from the H_2-data again being slightly higher (as was the case for B_2H_6 in the previous section). The pre-

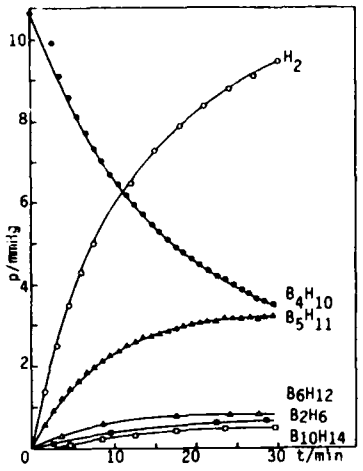


Fig. 1. Reaction profile for thermolysis of B_4H_{10} at 10.7 mmHg and 78 °C

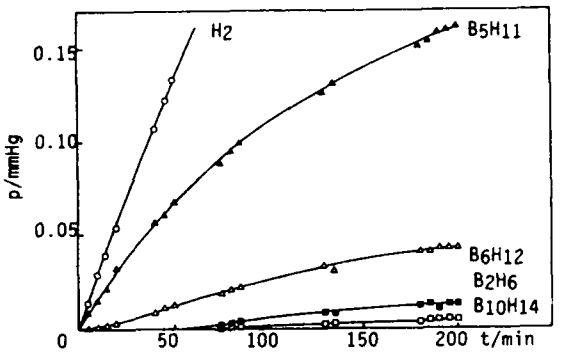


Fig.2. Reaction profile at high spectrometer gain showing build-up of the volatile boranes during the initial stages of thermolysis of B_4H_{10} at 3.9 mmHg and 40.2 °C

exponential factor for the first-order disappearance of B_4H_{10} was $A \approx 6 \times 10^{11}$ s^{-1}. These results are plotted in Fig. 3 together with earlier data from Schaeffer's group on the cothermolyses of B_4H_{10} with B_2H_6 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).

$$\{B_4H_8\} + B_4H_{10} \longrightarrow B_5H_{11} + \{B_3H_7\} \quad (6)$$

$$\{B_3H_7\} + \{B_3H_7\} \longrightarrow \{'B_6H_{14-2m}'\}_{(polymerizes)} + mH_2 \quad (7a)$$

$$\{B_3H_7\} + \{B_3H_7\} \longrightarrow B_4H_{10} + \{'B_2H_4'\}_{(polymerizes)} \quad (7b)$$

In addition to the initial homogeneous gas-phase decomposition of B_4H_{10} to H_2 and B_5H_{11} (equations 5a and 6) and the formation of solid 'polymer', other boranes (first B_6H_{12} then B_2H_6 and $B_{10}H_{14}$) are formed after various periods of induction (Fig. 2 above). Others (refs. 5 and 29) have suggested that B_6H_{12} might result from the interaction of two $\{B_3H_7\}$ fragments but in the present system the observed induction period suggests that it is more likely to arise from a cothermolysis reaction involving B_5H_{11}. Likewise, the virtual absence of B_2H_6 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, $\{B_3H_7\}$ [formed in reaction (6)] does not react with B_4H_{10} to give B_5H_{11} and B_2H_6, or with $\{B_4H_8\}$ to give B_5H_9 and B_2H_6, or with itself to give $\{B_4H_8\}$ and B_2H_6, though all these reactions have previously been proposed (ref. 5). Likewise, the self-reaction of $2\{B_4H_8\}$ to form either B_6H_{10} and B_2H_6 or B_5H_9 and $\{B_3H_7\}$ are also ruled out on this basis, and their reaction to form, B_5H_{11} and $'B_3H_5(polymer)'$, for which their 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 B_4H_{10}.

One further consequence of the recognition of reaction (5a) as the rate-determining step in the thermolysis of B_4H_{10} is the corollary that an excess of H_2 should inhibit the decomposition of B_4H_{10} and increase proportionately its conversion to B_5H_{11} and B_2H_6 [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 B_4H_{10} (3.5 mmHg) and H_2 (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 B_4H_{10} 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).

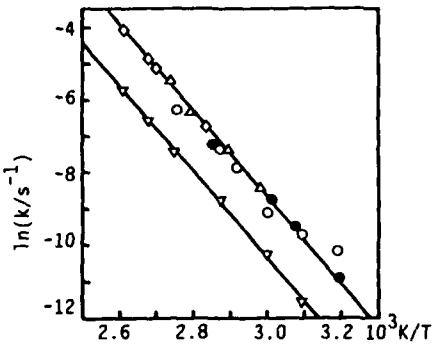


Fig.3. Arrhenius plot for thermolysis of B_4H_{10} alone ●, with CO ◇ (ref. 2e) with B_2H_6 △ (ref. 2a) and with B_6H_{10} ○. The lower set of points ▽ refers to thermolysis of B_4H_{10} in the presence of an excess of H_2

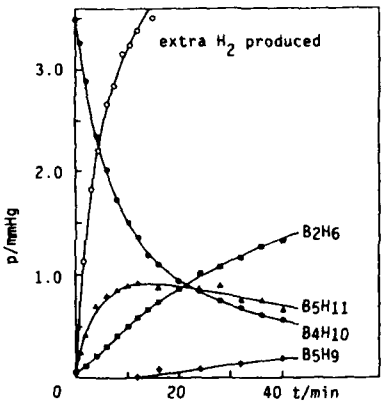


Fig. 4. Reaction profile for the cothermolysis of a mixture of B_4H_{10} (3.5 mmHg) and H_2 (20 mmHg) at 100 °C; the curve for H_2 represents the extra H_2 generated during the reaction

The detailed product analysis of this cothermolysis of (B_4H_{10} + $6H_2$) is illustrated by the typical reaction profile in Fig. 4 : the relative rates of B_5H_{11} production to B_4H_{10} consumption are unaltered from those of the thermolysis of B_4H_{10} alone, whereas there is a marked increase in the relative rate of production of B_2H_6 and almost complete inhibition of 'polymer' formation. The most striking effect is the complete absence of volatile higher boranes such as B_6H_{12} and $B_{10}H_{14}$.

All the effects of added H_2 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 B_5H_{11} via reaction (6). The relative increase in the rate of production of B_2H_6 undoubtedly stems from the removal of the $\{B_3H_7\}$, concurrently formed in step (6), via (-3) and (-2) in conjunction with (-1). The rapid removal of $\{B_3H_7\}$ likewise explains both the inhibition of polymer formation via reaction (7a) and/or (7b), and also the inhibition of B_6H_{12} formation, which probably arises in the normal thermolysis via reactions (8) and/or (9):

$$\{B_3H_7\} + B_5H_{11} \longrightarrow B_6H_{12} + B_2H_6 \qquad (8)$$

$$\{B_4H_8\} + B_5H_{11} \longrightarrow B_6H_{12} + \{B_3H_7\} \qquad (9)$$

For reasons already outlined the alternative suggested route to B_6H_{12} (namely $2\{B_3H_7\} \longrightarrow B_6H_{12} + H_2$) seems less likely though this would also be suppressed by added H_2.

THERMOLYSIS OF B_5H_{11} ALONE AND WITH ADDED H_2

Although there have been several reports in the past of qualitative studies dealing with the thermolysis of B_5H_{11} (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 B_5H_{11} at pressures of 1.8-10.4 mmHg and temperatures in the range 60-150 °C is found to be first-order in B_5H_{11} with an activation energy of 73.2±3.7 kJ mol^{-1} and a pre-exponential factor of 1.65×10^7 s^{-1}. The main volatile products are H_2 and B_2H_6, and these appear at rates of approximately 1 and 0.5 mole per mole of B_5H_{11} consumed. A small 'steady-state' concentration of B_4H_{10} is also present but, in agreement with the earlier work of Burg and Schlesinger (ref. 30), B_5H_9 is not detected in the initial stages. Others have claimed that B_5H_9 is formed from the outset (refs. 15b and 19) but we find that it builds up rather slowly as the reaction proceeds. $B_{10}H_{14}$ 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),

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

and our own observations are entirely consistent with this being the rate-determining step. The initial rate of production of B_2H_6 is then readily explained by its formation from $\{BH_3\}$

via reaction (-1) in ca. 100% yield. The fate of the {B_4H_8} produced in reaction (10) is less obvious. Long has conjectured (ref. 5) that it may react with itself to produce {B_3H_7} and B_5H_9, and subsequently with the {B_3H_7} to produce B_2H_6 and more B_5H_9. This would account for the B_5H_9, 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 B_4H_{10} thermolysis, in which {B_4H_8} features prominently. Lipscomb has calculated that the reaction of {B_4H_8} with B_5H_{11} to give B_4H_{10} is exothermic by 125.5 kJ mol^{-1}, and has suggested that this may be an important route to B_5H_9 (ref 4c). As Lipscomb has pointed out, at the temperatures required to decompose B_5H_{11}, B_4H_{10} would be decomposed to {B_4H_8} and H_2, so that {B_4H_8} is essentially a catalyst for the loss of H_2 from B_5H_{11} in this reaction. Whilst this reaction may contribute to the production of B_5H_9 and B_4H_{10} in this thermolysis, it is clear from the evidence that it is not a major sink for the {B_4H_8} produced in reaction (10). An alternative possibility is that {B_4H_8} and B_5H_{11} react to form n-B_9H_{15} via reaction (11). An advantage of this step is that it would nicely explain the

$$\{B_4H_8\} + B_5H_{11} \longrightarrow \text{n-}B_9H_{15} + 2H_2 \qquad (11)$$

observed very high initial production of H_2. The n-B_9H_{15} is presumed to be unstable under the prevailing conditions, decomposing via B_8H_{12} (see later) to produce 'polymer' and $B_{10}H_{14}$. Reaction (11) was used by Long (ref. 5) to explain the observation (ref. 32) that n-B_9H_{15} is the main product when B_5H_{11} and B_2H_6 are held together under pressure at room temperature for a few days. The B_2H_6 in this reaction was regarded as playing the dual role of increasing the {B_4H_8} concentration by syphoning off the {BH_3} molecules formed in (10), and stabilizing the n-B_9H_{15} via the reversible reaction with B_8H_{12} (ref. 5). We intend to test the possibility that reaction (11) is operative, by thermolysing B_5H_{11} under hot/cold conditions in an attempt to stabilize the n-B_9H_{15} as it is formed.

It is of interest to compare the Arrhenius parameters for B_5H_{11} with those for B_4H_{10}, and to consider the wider implications of the results. The value of 6×10^{11} s^{-1} recorded above for the pre-exponential factor for B_4H_{10} is reasonable for a unimolecular reaction (ref. 33) and is consistent with the proposed mechanism in which H_2 is ejected via a loosely bound transition state. The value for B_5H_{11} is lower by more than 4 orders of magnitude (1.6×10^{7} s^{-1}) and this inmplies considerable re-organization to a tightly bound transition state. This is consistent with the more dramatic structural changes which accompany the release of a BH_3 group from the cluster , and it will be of interest to see whether this behaviour is mirrored in the B_6H_{12} thermolysis, which we are also currently investigating. The considerably greater activation energy for B_4H_{10} compared with that for B_5H_{11} reflects a more dramatic temperature dependence of the rate constant for the former, and, from the initial rate laws, the ratio $k_{B_4H_{10}}/k_{B_5H_{11}}$ 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 B_5H_{11} produced in the thermolysis of B_4H_{10} is only slightly less than the rate of decomposition of B_4H_{10} 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 B_5H_{11} builds up to the extent that it does in the B_4H_{10} thermolysis, but it must be remembered that both {B_4H_8} and {BH_3}, the initial products of the decomposition of B_5H_{11} [see reaction (10)], themselves react further with B_4H_{10} to regenerate B_5H_{11} [reactions (6) and (-12)].

It has often been suggested (refs. 2a, 22, 30) that B_5H_{11} and B_4H_{10} are interconvertible in the presence of H_2, according to the 'equilibrium' (12). However, it was not clear whether

$$B_5H_{11} + H_2 \rightleftharpoons \tfrac{1}{2}B_2H_6 + B_4H_{10} \qquad (12)$$

the forward reaction (12) occurred as a single step (i.e. BH abstraction by H_2 from B_5H_{11} to give {BH_3}) 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 B_5H_{11} in the presence of added H_2 over a wide range of temperature (ref. 21). The rate of thermolysis was found to be largely unaffacted by the presence of an excess of H_2 (see Fig. 5), suggesting that the rate-determining step remains the same, i.e. reaction (10).

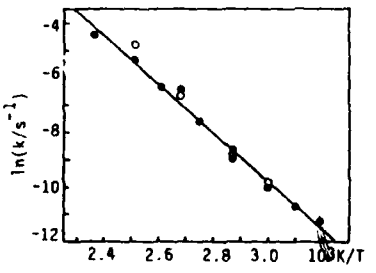


Fig. 5. Arrhenius plot for thermolysis of B_5H_{11} at a pressure of 3.5 mmHg alone ●, and with 50 mmHg added H_2 o

THERMOLYSIS AND COTHERMOLYSIS REACTIONS OF B_6H_{10}

A particularly intriguing aspect of the thermolysis of B_2H_6 is the virtual absence of hexaboranes and other species intermediate between the pentaboranes and $B_{10}H_{14}$. Schaeffer has suggested (ref. 2j) that B_6H_{10} 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 $\{BH_3\}$, $\{B_3H_7\}$, $\{B_4H_8\}$, B_8H_{12}, and $\{B_9H_{13}\}$ to produce larger boranes such as $B_{13}H_{19}$, $B_{14}H_{22}$, and $B_{15}H_{23}$. Just how important this role is will depend on the extent to which B_6H_{10} is actually produced in the B_2H_6 decomposition, and at present this is simply not known. Under certain conditions $\{BH_3\}$ can react with B_5H_9 to produce a hexaborane (ref. 3d), though this was not specifically identified as B_6H_{10}, and Long (ref. 5) has proposed several possible routes involving the reactive intermediates $\{B_3H_7\}$ and $\{B_4H_8\}$ e.g. $\{B_3H_7\} + B_5H_9 \longrightarrow B_2H_6 + B_6H_{10}$, $2\{B_4H_8\} \longrightarrow B_2H_6 + B_6H_{10}$, and $\{B_4H_8\} + B_5H_9 \longrightarrow \{B_3H_7\} + B_6H_{10}$. It is also established that B_8H_{12} decomposes *via* the first-order reaction (13) to give B_6H_{10} and solid polymer (ref. 2g). We are at present

$$B_8H_{12} \longrightarrow B_6H_{10} + B_2H_2 \text{ (polymerizes)} \qquad (13)$$

devising ways of testing some of these steps experimentally, but in the meantime, to establish the likely behaviour of B_6H_{10} 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 B_6H_{10} 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 4.7×10^6 m^3 mol^{-1} s^{-1} (ref. 14). In the initial stages a typical reaction produces 1 mole of H_2 per mole of B_6H_{10} 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 H_2 to give an insoluble, intractable solid of composition BH_x (where x is ~1.0). Minor amounts of B_5H_9 and $B_{10}H_{14}$ in an approximate molar ratio of 5:1 are also produced. B_2H_6, B_8H_{12}, B_9H_{15}, as well as B_{13}, B_{14}, and B_{15} 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 H_2, and a minor route producing B_5H_9 and $B_{10}H_{14}$. 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 B_6H_{10}, and the main task was to deduce the fate of the activated complex $\{B_{12}H_{20}\}^{\ddagger}$. Such a scheme was devised (ref. 14) leading to an overall stoichiometry for this minor route of $5B_6H_{10} \longrightarrow 4B_5H_9 + B_{10}H_{14}$. Notwithstanding the good agreement between the predicted B_5H_9:$B_{10}H_{14}$ 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 $B_{24}H_{30}$, which appears to be the *conjuncto* dimer of the recently identified molecule $B_{12}H_{16}$ (ref. 37).

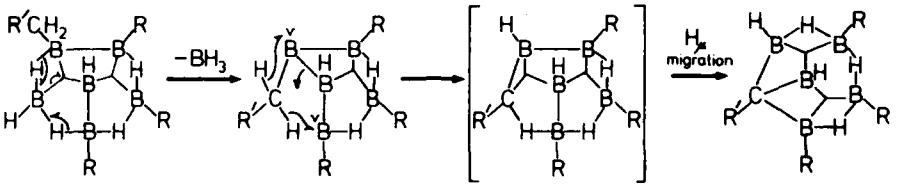
Surface studies (ref. 36)

To check for a possible heterogeneous component in the reaction rates, a thermolysis of B_6H_{10} 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, $(CF_2)_n$, 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 B_6H_{10} required careful investigation.

Cothermolysis of B_6H_{10} with ethene and propene (ref. 36)

Ethene and propene are well known 'radical scavengers' (ref. 33). With B_6H_{10} 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 B_6H_{10} (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 $R'CB_5H_{8-x}R_x$ (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 $EtCB_5H_{8-x}Pr_x$ (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 $R'CB_5H_{8-x}R_x$ (x = 0-3) by elimination of {BH_3} from $R'CH_2B_6H_{9-x}R_x$ (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-isolable 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:

$$B_6H_{10} + B_6H_{10} \longrightarrow 2B_6H_9^{\cdot} + H_2 \qquad \text{Initiation}$$

$$B_6H_9^{\cdot} + B_6H_{10} \longrightarrow (B_6H_8)_2H^{\cdot} + H_2$$

$$(B_6H_8)_nH^{\cdot} + B_6H_{10} \longrightarrow (B_6H_8)_{n+1}H^{\cdot} + H_2$$

$$(B_6H_8)_nH^{\cdot} + B_6H_{10} \longrightarrow (B_6H_8)_{n+1} + H_2 + H^{\cdot} \qquad \text{Propagation}$$

$$H^{\cdot} + B_6H_{10} \longrightarrow B_6H_9^{\cdot} + H_2$$

$$(B_6H_8)_nH^{\cdot} + (B_6H_8)_mH^{\cdot} \longrightarrow (B_6H_8)_{n+m}H_2 \qquad \text{Termination}$$

When n is large the overall stoichiometry is seen to be

$$nB_6H_{10} \longrightarrow (B_6H_8)_n + nH_2$$

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 $B_{13}H_{19}$, $B_{14}H_x$, $B_{15}H_{23}$ 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 B_6H_{10}.

The observation that the alkylhexaborane-carbaborane conversion can occur readily only when $\{BH_3\}$-release is possible, inevitably raises the question as to whether B_6H_{10} itself can release $\{BH_3\}$ in this way, i.e. *via* reaction (14). In fact there is good evidence that this

$$B_6H_{10} \longrightarrow \{B_5H_7\} + \{BH_3\} \qquad (14)$$

may well be the route to the minor products of the B_6H_{10} 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 B_5H_9 and $B_{10}H_{14}$ could arise from the reactive intermediate $\{B_5H_7\}$, the former *via* its reaction with the H_2 produced in the main reaction, and the latter *via* its self-association. The $\{BH_3\}$ produced in reaction (14) would probably form B_2H_6, which in cothermolysis with B_6H_{10} would immediately give $B_{10}H_{14}$ (see later). In the cothermolysis of B_6H_{10} 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 $\{BH_3\}$ eliminated in the conversion of the alkylated hexaboranes to the monocarbaboranes, but also from that produced in reaction (14).

Cothermolysis of B_6H_{10} with other boranes (ref. 21)

Having established the nature of the B_6H_{10} self-thermolysis, preliminary cothermolysis reactions were attempted with B_2H_6, B_4H_{10}, B_5H_9, and B_5H_{11}. In all cases except B_5H_9, the rate of consumption of B_6H_{10} was found to be more rapid than in the self-thermolysis, clearly indicating that interactions were occurring. Detailed kinetic studies with B_2H_6 and B_4H_{10} showed that in each case the rate was governed by the rate-determining sequence of the co-reactant. Thus with B_2H_6 the reaction was found to be 3/2-order in B_2H_6 and zero order in B_6H_{10}, whereas with B_4H_{10} the reaction was first-order in B_4H_{10} and zero-order in B_6H_{10}. The rate data for disappearance of B_2H_6 and B_4H_{10} (see Fig. 3) when cothermolysed with B_6H_{10} are compatible with the Arrhenius plots for the self-reactions of these boranes. Thus, the activation energy, E_A, for cothermolysis of B_6H_{10}/B_2H_6 is 98.8±3.9 kJ mol^{-1} compared with 92.3±6.6 kJ mol^{-1} for thermolysis of B_2H_6 alone, and E_A for B_6H_{10}/B_4H_{10} is 88.4±6.1 kJ mol^{-1} compared with 99.2±0.8 kJ mol^{-1} for B_4H_{10} alone.

In the B_6H_{10}/B_2H_6 cothermolysis the main volatile product apart from H_2 was found to be $B_{10}H_{14}$ in yields of up to 40%. Despite the fact that the B_2H_6 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 B_6H_{10} and either B_2H_6 itself or $\{BH_3\}$. Instead it seems likely that B_6H_{10} reacts with $\{B_3H_7\}$, the product of the rate-determining step (3), to give B_9H_{15} *via* reaction (15). This step has

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

been proposed in the past, without direct evidence (ref. 5), and it has been shown that B_6H_{10} reacts with $^{10}B_3H_7.THF$ at 0 °C in the presence of BF_3 to give B_9H_{15} labelled at the 3, 4, and 9 positions (ref. 35b). If B_9H_{15} is formed, it must then decompose immediately to $B_{10}H_{14}$. 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 B_9H_{15} and $^{10}B_2H_6$, the resulting $B_{10}H_{14}$ has two labelled boron atoms, implying that the route is *via* B_8H_{12}. 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 B_6H_{10} reacts *via* reaction (15).

$$B_9H_{15} \longrightarrow B_8H_{12} + \{BH_3\} \qquad (16)$$

$$\{B_3H_7\} + B_8H_{12} \longrightarrow \{B_9H_{13}\} + B_2H_6 \qquad (17)$$

$$\{B_3H_7\} + \{B_9H_{13}\} \longrightarrow B_{10}H_{14} + B_2H_6 \qquad (18)$$

It is possible that the B_2H_6 decomposition proceeds as far as the production of $\{B_4H_8\}$ [reactions (4) and (5a)] before the interaction with B_6H_{10} occurs to give $B_{10}H_{14}$, but results discussed later suggest that this is not the case.

In the B_6H_{10}/B_4H_{10} cothermolysis, B_9H_{15} 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 B_2H_6 and B_6H_{10}. A similar result has been

obtained in the reaction at much lower temperatures between B_4H_8CO and B_6H_{10} (ref. 35b), and it seems reasonable to invoke reaction (19) in each case. In this respect it is clear that

$$\{B_4H_8\} + B_6H_{10} \longrightarrow B_9H_{15} + \{BH_3\} \qquad (19)$$

the previously proposed (ref. 5) reaction of these two species to give $2B_5H_9$ 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 B_6H_{10} and the reaction intermediates $\{B_3H_7\}$ and $\{B_4H_8\}$. In the B_6H_{10}/B_2H_6 cothermolysis, B_6H_{10} is in competition with B_2H_6 for the $\{B_3H_7\}$ [reactions (4) and (15)], whereas in the B_6H_{10}/B_4H_{10} cothermolysis, it competes successfully with B_4H_{10} for $\{B_4H_8\}$ [reactions (6) and (19)]. To test these competitive effects further, the effect of adding an excess of H_2 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 H_2, confirming that the respective rate-determining sequences were unaltered, but retardation was observed only in the B_6H_{10}-B_4H_{10} case. In view of the fact that both the B_2H_6 and B_4H_{10} self-reactions are retarded by the presence of added H_2 [presumably *via* reactions (-3) and (-5a), respectively], the lack of inhibition in the $B_6H_{10}/B_2H_6/H_2$ system, even in the presence of a 10-fold excess of added H_2, demonstrates that B_6H_{10} is particularly effective in its competition for $\{B_3H_7\}$. Returning to an earlier point, it is now clear that B_6H_{10} does in fact react, in the B_6H_{10}/B_2H_6 cothermolysis, at the $\{B_3H_7\}$ 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 B_2H_6 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 B_2H_6/D_2 exchange reaction and from measurements of the quantum yield of BH_3 [$\phi(BH_3) = 2.0 \pm 0.25$] it was concluded that the primary photochemical step is the same as that proposed in thermolysis: $B_2H_6 + h\nu \longrightarrow 2\{BH_3\}$. 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 B_5H_9 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 B_2H_6, B_4H_{10}, and B_5H_9 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_2H_6	B_4H_{10}	P_5H_9	B_5H_{11}	B_6H_{10}	B_6H_{12}	$n\text{-}B_9H_{15}$	$B_{10}H_{14}$
λ_{max}/nm	<195	<195	<195	209	247	263	260	272
$\varepsilon/m^2\ mol^{-1}$	2.0[a]	0.71[a]	88[a]	82.9	165.1	278.9	~200[b]	248.6[c]

[a]Data refer to ε at 195 nm; λ_{max} is at shorter wavelengths
[b]Approx. value: sample decomposed during measurement
[c]In hexane solution

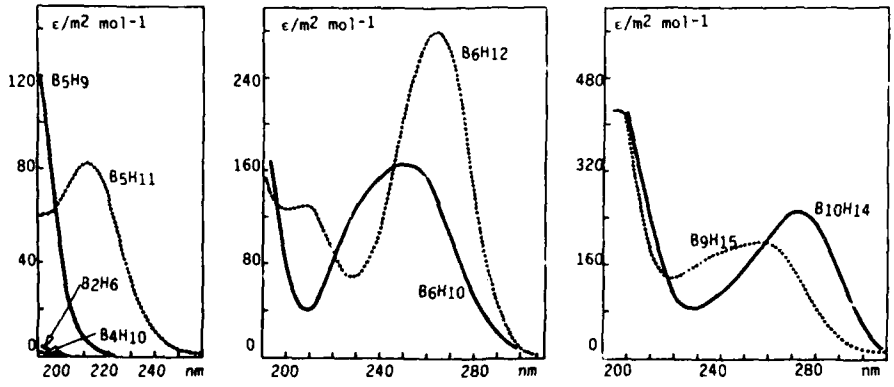


Fig. 6. UV absorption spectra of gaseous boranes ($B_{10}H_{14}$ in hexane solution)

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_2H_6 and B_5H_9 as the main product boranes:

$$B_6H_{12} \longrightarrow B_5H_9 + \{BH_3\} \qquad (19)$$

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 subtantially 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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