# Kinetics and mechanism of the thermolysis and photolysis of binary boranes

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<u>Abstract</u> - 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  $566\pm15$  kJ mol<sup>-1</sup>.

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,  $\overline{E}$  for B-B in boranes and C-C in C2H6 are essentially the same ( $_{332}$  kJ mol<sup>-1</sup>); likewise the value of 380 kJ mol<sup>-1</sup> for BBB(3c,2e) is similar to that for  $\overline{E}$ (B-C) in BMe3 (372 kJ mol<sup>-1</sup>). The value of

∆H°f,298/kJ mol <sup>-1</sup> (refs.8,9)		Ē(X-Y)/kJ m	ol <sup>-1</sup> (ref. 9)	$\overline{E}(X-Y)/kJ \text{ mol}^{-1}$ (refs. 8,10)		
H(g) B(g)	<sup>1</sup> ⁄ <sub>2</sub> x436 566	B-B(2c,2e) BBB(3c,2e)	332 380	C-C B-C	331 <sup>a</sup> 372 <sup>b</sup>	
C(g)	356	B-H(2c,2e) BHB(3c,2e)	381 441	С-Н Н-Н	416 436	

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

<sup>a</sup>Value derived for C-Me in C2H6; this is slightly lower than the value of 356 kJ <sup>b</sup>mol<sup>-1</sup>for the heat of atomization of diamond. <sup>b</sup>Value derived for B-Me in BMe3; similar values are obtained from BEt3, BBu3, and

Value 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<sup>-1</sup>): this has been ascribed to additional  $p_{\pi}$ -bonding (ref. 11).

381 kJ mol<sup>-1</sup> for  $\overline{E}(B-H)$  is also similar, though slightly less than that for  $\overline{E}(C-H)$  (416 kJ mol<sup>-1</sup>) whereas the value for BHB(3c,2e) is slightly greater than the values for  $\overline{E}(C-H)$  (in CH4) and 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, 3/2, 2, 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 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:

$$B_2H_6 \implies 2\{BH_3\}$$
(1)

$$\{BH_3\} + B_2H_6 \Longrightarrow \{B_3H_9\}$$
(2)

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

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 10<sup>3</sup>-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 EA was 92.3±6.6 kJ mol<sup>-1</sup> and the preexponential factor A was 1.58x108 m3/2 mol<sup>-1/2</sup> s<sup>-1</sup>. The correponding Arrhenius parameters from the initial rates of H2 production were somewhat higher (EA =113.0±7.3 kJ mol<sup>-1</sup> and A = 3.08x1010 m3/2 mol<sup>-1/2</sup> s<sup>-1</sup>) 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 H<sub>2</sub> is known to inhibit the decomposition of B<sub>2</sub>H<sub>6</sub> (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<sub>2</sub>H<sub>6</sub> 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<sub>2</sub>. Further quantitative work is planned in this area.

### THERMOLYSIS OF B<sub>4</sub>H<sub>10</sub> AND ITS EXCHANGE WITH D<sub>2</sub>

There is now little doubt that  $B4H_{10}$  is the first isolable species in the thermolysis of  $B_{2H6}$  (ref. 2c). It is formed via reaction (4), though under normal thermolytic conditions

$$B_{3}H_{7}$$
 +  $B_{2}H_{6} \longrightarrow B_{4}H_{10} + \{BH_{3}\}$  (4)

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):

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

$$B_4H_{10} \longrightarrow \{B_3H_7\} + \{BH_3\}$$
 (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  $D_2$  (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  $\longrightarrow$  {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 EA(B4H10) = 99.2±0.8, EA(B5H11) = 98.8±1.8, and EA(H2) = 107.5±1.9 kJ mol<sup>-1</sup>, 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 x1011 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).

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

$${}^{B_{3}H_{7}} + {}^{B_{3}H_{7}} \longrightarrow {}^{B_{6}H_{14-2m'}}_{(polymerizes)} + {}^{mH_{2}}$$
(7a)

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

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 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 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 (rets. 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  ${\sim}5$  (ref. 21). These observations provide cogent additional evidence that  $B4H_{10}$  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 B4H10 alone  $\bullet$ , with CO  $\diamond$  (ref. 2e) with B2H6  $\triangle$ (ref. 2a) and with B6H10 o. The lower set of points  $\bigtriangledown$  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 H<sub>2</sub> (20 mmHg) at 100 °C; the curve for H<sub>2</sub> represents the extra H<sub>2</sub> generated during the reaction

The detailed product analysis of this cothermolysis of  $(B4H_{10} + 6H_2)$  is illustrated by the typical reaction profile in Fig. 4 : the <u>relative</u> rates of B5H11 production to B4H10 consumption are unaltered from those of the thermolysis of B4H10 alone, whereas there is a marked <u>increase</u> 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 H<sub>2</sub> 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 <u>via</u> 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 reaction (7a) and/or (7b), and also the inhibition of B6H12 formation, which probably arises in the normal thermolysis <u>via</u> reactions (8) and/or (9):

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

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

For reasons already outlined the alternative suggested route to B6H12 (namely  $2{83H7} \longrightarrow B6H12 + H2$ ) 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  $73.2\pm3.7$  kJ mol<sup>-1</sup> and a pre-exponential factor of  $1.65\times107$  s<sup>-1</sup>. The main volatile products are H<sub>2</sub> 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 B5H<u>9 is</u> 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),

$$_{5}^{H_{11}} = \{B_{4}^{H_{8}}\} + \{B_{4}^{H_{8}}\}$$

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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  $\{\mathsf{BH3}\}$ 

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(10)

<u>via</u> reaction (-1) in <u>ca</u>. 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 <u>direct</u> 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<sup>-1</sup>, 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 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

$$[B_{4}H_{8}] + B_{5}H_{11} \longrightarrow \underline{n} - B_{9}H_{15} + 2H_{2}$$
 (11)

observed very high initial production of H<sub>2</sub>. The <u>n</u>-B9H15 is presumed to be unstable under the prevailing conditions, decomposing <u>via</u> B8H12 (see later) to produce 'polymer' and B10H14. Reaction (11) was used by Long (ref. 5) to explain the observation (ref. 32) that <u>n</u>-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 <u>n</u>-B9H15 <u>via</u> 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 <u>n</u>-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  $B5H_{11}$  is lower by more than 4 orders of magnitude (1.6x107  $s^{-1}$ ) 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 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 kB4H10/kB5H11 is found to vary from  $\sim$ 48.9 at 200 °C to  $\sim$ 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  $B5H_{11}$  and  $B4H_{10}$  are interconvertible in the presence of H<sub>2</sub>, according to the 'equilibrium' (12). However, it was not clear whether

$$B_5H_{11} + H_2 \longrightarrow \frac{1}{2}B_2H_6 + B_4H_{10}$$

the forward reaction (12) occurred as a single step (i.e. BH abstraction by H2 from B5H11 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 B5H11 in the presence of added H2 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 H2 (see Fig. 5), suggesting that the rate-determining step remains the same, i.e. reaction (10).

Fig. 5. Arrhenius plot for thermolysis of  $B5H_{11}$  at a pressure of 3.5 mmHg alone  $\bullet$ , and with 50 mmHg added H<sub>2</sub> o



## THERMOLYSIS AND COTHERMOLYSIS REACTIONS OF B<sub>6</sub>H<sub>10</sub>

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} + B5H9  $\longrightarrow$  {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

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

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  $79.7\pm2.7$  kJ mol<sup>-1</sup> and a pre-exponential factor of  $4.7\times106$  m<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> (ref. 14). In the initial stages a typical reaction produces 1 mole of H<sub>2</sub> 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 BH1.33, which then loses more H<sub>2</sub> to give an insoluble, intractable solid of composition BH<sub>x</sub> (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 H<sub>2</sub>, 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  $\{B12H20\}^{\ddagger}$ . Such a scheme was devised (ref. 14) leading to an overall stoichiometry for this minor route of 5B6H10  $\longrightarrow$  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 C0 (to be reported elsewhere) and thermolytic experiments leading to the isolation of a new borane B24H30, which appears to be the <u>conjuncto</u> 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  $153 \,^{\circ}\text{C}$  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 <u>decreased</u> 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)<sub>n</sub>, 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 B<sub>6</sub>H<sub>10</sub> 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 <u>ca</u>. 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  $B_{0-xR_x}$  (R = Et or Pr, x = 1-5), many of which are new compounds. These are followed by the series of alkylated monocarbaboranes R'CB5H8-xRx (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  $B_{0-xPx}$  (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 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'CB5H8-xRx (x = 0-3) by elimination of {BH3} from R'CH2B6H9-x Rx (x = 0-3). (R = Et or H, R' = Me; R = Pr or H, R' = Et)

In the case of the penta-alkylated species, {BH3} release is precluded and the formation of the monomonocarbaborane inhibited. Its virtual absence also indicates that hydroboration of the monocarbaboranes themselves does not occur. In the presence of alkene, {BH3} is readily hydroborated, which accounts (in part) for the appearance of boron trialkyls.

#### Mechanism of B<sub>6</sub>H<sub>10</sub> 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 B6H10 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 {BH3}, {B3H7}, or {B4H8}. 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 B5H9 (ref. 38) and B10H14 (ref. 39) may also decompose via radical intermediates, but detailed evidence is lacking. The initial products of the B6H10/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 B6H9°. In the absence of 'trapping' agents, this species will react further with B6H10, 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 B6H10 is thus:

<sup>B</sup> 6 <sup>H</sup> 10 <sup>+ B</sup> 6 <sup>H</sup> 10	>	<sup>2B</sup> 6 <sup>H</sup> 9 <sup>•</sup> + <sup>H</sup> 2	Initiation
<sup>B</sup> 6 <sup>H</sup> 9 <sup>•</sup> + <sup>B</sup> 6 <sup>H</sup> 10	>	(B <sub>6</sub> H <sub>8</sub> ) <sub>2</sub> H• + H <sub>2</sub>	ן
(B <sub>6</sub> H <sub>8</sub> ) <sub>n</sub> H <sup>•</sup> + B <sub>6</sub> H <sub>10</sub>	>	(B <sub>6</sub> H <sub>8</sub> ) <sub>n+1</sub> H <sup>•</sup> + H <sub>2</sub>	Propagation
(B <sub>6</sub> H <sub>8</sub> ) <sub>n</sub> H <sup>•</sup> + B <sub>6</sub> H <sub>10</sub>	>	(B <sub>6</sub> H <sub>8</sub> ) <sub>n+1</sub> + H <sub>2</sub> + H	·
H' + B <sub>6</sub> H <sub>10</sub>	>	<sup>B</sup> 6 <sup>H</sup> 9 <sup>•</sup> + <sup>H</sup> 2	]
(B <sub>6</sub> H <sub>8</sub> ) <sub>n</sub> H <sup>•</sup> + (B <sub>6</sub> H <sub>8</sub> ) <sub>m</sub> H <sup>•</sup>	>	(B <sub>6</sub> H <sub>8</sub> ) <sub>n+m</sub> H <sub>2</sub>	Termination

When n is large the overall stoichiometry is seen to be

 $^{nB_{6}H_{10}} \longrightarrow (^{B_{6}H_{8}})_{n} + ^{nH_{2}}$ 

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  $B_6H_9$  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  $B_{13}H_{19}$ ,  $B_{16}H_{23}$  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  $B_{6}H_{10}$ .

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

$$B_{6}H_{10} \longrightarrow \{B_{5}H_{7}\} + \{BH_{3}\}$$
 (14)

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 $B_6H_{10}$ 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, EA, for cothermolysis of B6H10/B2H6 is 98.8±3.9 kJ mol<sup>-1</sup> compared with 92.3±6.6 kJ mol<sup>-1</sup> for thermolysis of B2H6 alone, and EA for B6H10/B4H10 is 88.4±6.1 kJ mol<sup>-1</sup> compared with 99.2±0.8 kJ mol<sup>-1</sup> 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 <u>no</u> 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 <u>via</u> reaction (15). This step has

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

been proposed in the past, without direct evidence (ref. 5), and it has been shown that B6H10 reacts with  $10B_{3H7}$ .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  $10B_{2H6}$ , the resulting B10H14 has two labelled boron atoms, implying that the route is <u>via</u> 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).

$$B_{g}H_{15} \longrightarrow B_{g}H_{12} + \{BH_{3}\}$$

$$(16)$$

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

$$\{B_{3}H_{7}\} + \{B_{9}H_{13}\} \longrightarrow B_{10}H_{14} + B_{2}H_{6}$$
 (18)

It is possible that the  $B_{2H6}$  decomposition proceeds as far as the production of { $B_{4H8}$ } [reactions (4) and (5a)] before the interaction with  $B_{6H10}$  occurs to give  $B_{10H14}$ , but results discussed later suggest that this is not the case.

In the  $B6H_{10}/B4H_{10}$  cothermolysis,  $B9H_{15}$  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  $B_{2}H_{6}$  and  $B_{6}H_{10}$ . 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

(19)

$$\{B_{4}H_{8}\} + B_{6}H_{10} \longrightarrow B_{9}H_{15} + \{BH_{3}\}$$

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 [ $\phi$ (BH3) = 2.0  $\pm$  0.25] it was concluded that the primary photochemical stee is the same as that proposed in thermolysis: B2H6 + hv  $\longrightarrow$  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 <u>conjuncto</u>-icosaborane(26) (ref. 43). Recent work involving the cophotolysis of binary boranes such as B5H9 with other gas-phase species such as hexafluoro-acetone 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 11 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.

Borane	<sup>B</sup> 2 <sup>H</sup> 6	$B_4H_{10}$	<sup>B</sup> 5 <sup>H</sup> 9	<sup>8</sup> 5 <sup>H</sup> 11	<sup>B</sup> 6 <sup>H</sup> 10	<sup>B</sup> 6 <sup>H</sup> 12	<sup>n-B</sup> 9 <sup>H</sup> 15	<sup>B</sup> 10 <sup>H</sup> 14	-
$\lambda_{max}/nm$	<195	<195	<195	209	247	263	260	272	
$\epsilon/m^2 mol^{-1}$	2.0 <sup>a</sup>	0.71 <sup>a</sup>	88 <sup>a</sup>	82.9	165.1	278.9	∿200 <sup>b</sup>	248.6 <sup>C</sup>	

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

Data refer to  $\varepsilon$  at 195 nm;  $\lambda_{max}$  is at shorter wavelengths

Approx. value: sample decomposed during measurement

In hexane solution



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

In a series of photolyses  $B_{2}H_{6}$ ,  $B_{4}H_{10}$ , and  $B_{5}H_{9}$  were found to be much more stable than  $B_{5}H_{11}$ , BGH10, and BGH12 (ref. 36). For example, the initial rates of consumption of the bornace (in arbitrary units) were  $\sim 0$ , 0.33, 2.5, 50, 100, and 380 respectively, and the initial rates of production of H2 (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 B2H6-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  $B_{2H6}>B_{4H10}$ ,  $B_{5H9}>>B_{5H11}>B_{6H10}>B_{6H12}$ , in sharp contrast with the thermolytic stability of these boranes which follows the sequence B5H9>B2H6~B6H10>B6H12>B5H11 >B4H10. The most notable differences are for B4H10 (which is very stable to photolysis but very unstable thermally) and B6H10, for which the reverse applies. It is also noteworthy that the sequence of photolytic stability for the arachno series (B4H10>B5H11>B6H12) 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 B6H12 might well be the elimination of {BH3} to give B2H6 and B5H9 as the main product boranes:

$$B_6H_{12} \longrightarrow B_5H_9 + \{BH_3\}$$

Photolysis of B5H11 may also involve facile elimination of {BH3} as the initial step.

A kinetic study of the photolysis of B6H10 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 B6H10 were interpreted in terms of a bimolecular initiation. Under photolytic conditions at 0 °C, however, first-order kinetics are observed for both consumption of B6H10 and production of H2. As in thermolysis the main volatile product was H2 and most of the boron disappeared from the gas phase. However, a significant difference from thermolysis was that B2H6 appeared as the sole volatile borane and B5H9 was virtually absent. There was also subtantially less H2 produced proportionately in photolysis, the observed ratio of H2 produced per mole of B6H10 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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