Interconversion of Boron Hydrides. Part 2.[1] Cothermolysis of Tetraborane(10), B_4H_{10}, with Other Boranes at 75 °C

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A mass spectrometric method of analysis has been used to study the cothermolysis of B_4H_{10} with B_2H_6, B_5H_9, B_5H_{11}, B_6H_{10}, and B_6H_{12} at 75 °C. The reactions are complicated. The variations with time of the concentrations of the major products are compared with results obtained from the thermolysis of each borane singly to elicit information about the role of B_4H_{10} and possible reactive species formed from B_4H_{10} in the cothermolysis. A series of reactions are suggested which invoke $\{B_4H_8\}$ as a reactive species of major importance from B_4H_{10}.

We have recently developed a mass spectrometric method for the continuous quantitative analysis of borane mixtures.[1] As part of a general study of gas-phase interconversions of boranes we report here the use of the method in an initial, non-kinetic, investigation of cothermolyses of B_4H_{10} with B_2H_6, B_5H_9, B_5H_{11}, B_6H_{10}, and B_6H_{12}. By comparing the time variation of the concentrations of species during the cothermolysis with the results from the thermolysis of individual boranes, it has been possible to form some conclusions about the role played in interconversion reactions by B_4H_{10} and reactive species produced therefrom.

Evidence from both mass-spectrometrically analysed thermolysis studies [2-4] and chemical reactions [5] has led to the proposal of three highly reactive species in B_4H_{10} chemistry [reactions (1) and (2)]. Such species are

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

$$B_4H_{10} \rightleftharpoons \{B_3H_7\} + \{BH_3\} \qquad (2)$$

involved in most suggested mechanisms of borane interconversions, *e.g.* B_2H_6 thermolysis.[6] The importance of reaction (1) is worth noting since similar reactions are no longer regarded as significant for B_5H_{11} or B_6H_{12}, although there is evidence for loss of H_2 from B_9H_{15},[7] and loss of H_2 from $\{B_3H_9\}$ has often been conjectured.[6] The removal of a $\{BH_3\}$ group by reactions related to (2) has been reported for B_5H_{11} [8a] and B_9H_{15},[8b] and suggested for $\{B_3H_9\}$ and B_6H_{12}.[5] Stafford [3] has proposed that reaction (1) proceeds faster than (2) on the basis of his work on B_4H_{10} thermolysis. However, only at temperatures above 180 °C was evidence of $\{B_4H_8\}$ obtained and small quantities of $\{BH_3\}$ or $\{B_3H_7\}$ compared to $\{B_4H_8\}$ could not be excluded.[2]

EXPERIMENTAL

The preparation of boranes and the method of analysis of the mass spectra of mixtures have been discussed in Part 1.[1] For each cothermolysis reaction the reactants and argon were metered into a known volume and allowed to mix at room temperature for several minutes. The mixture was expanded into the reaction vessel which was then isolated. The spectrum of the mixture was recorded as previously described and the initial partial pressures of boranes (usually of the order of 3 mmHg) † and argon were calculated.[1] The reaction vessel was heated from room temperature to 75 °C in 3 min. The zero reaction time was taken 2 min after the start of heating. Spectra were recorded at set time intervals up to 120 min. At the end of each reaction high-resolution measurements were made to check the proportions of B_5H_9 and B_5H_{11}, and B_6H_{10} and B_6H_{12}, in the pentaborane and hexaborane regions of the spectra.[1] As with the previous work, no quantitative analyses of H_2 or solid polymeric boranes were attempted.

RESULTS AND DISCUSSION

Cothermolysis of B_2H_6 *and* B_4H_{10} *at* 75 °C.—The reactivity of both B_2H_6 and B_4H_{10} was increased in the cothermolysis compared to the thermolysis of each singly, the effect being more noticeable for B_2H_6, as shown in the Figure deposited in Supplementary Publication No. SUP 22542 (4 pp.).‡ In the cothermolysis after 120 min at 75 °C the concentration of B_2H_6 was reduced by almost 30% from its original value (3.3 mmHg) compared to a reduction of <8% after the same time in the thermolysis of B_2H_6 at 100 °C.[1] Further, it should be noted that B_2H_6 is itself produced on thermolysing B_4H_{10} at 75 °C to an extent of *ca.* 10% of the initial concentration of B_4H_{10} in 120 min.[1] In the cothermolysis the initial B_4H_{10} concentration (3.3 mmHg) decreased by *ca.* 93% compared to a decrease of 86% in thermolysis of B_4H_{10} alone.

By far the most abundant product was B_5H_{11}. Between 60 and 120 min after the reaction had started the concentration of B_5H_{11} was about three times that found in the thermolysis of B_4H_{10} alone, where again B_5H_{11} was the most abundant product. Other, comparatively minor, products were hexaboranes (B_6H_{10} and B_6H_{12} in a ratio of 2 : 3 from high-resolution measurements) and $B_{10}H_{14}$. These appeared at lower rates and in less abundance than from the thermolysis of B_4H_{10} singly.

The reaction (3) between B_2H_6 and B_4H_{10} to produce

$$2B_4H_{10} + B_2H_6 \rightleftharpoons 2B_5H_{11} + 2H_2 \qquad (3)$$

B_5H_{11} and H_2 has long been suggested to be an equilibrium.[9] A study of the kinetics of the forward reaction between 72.5 and 92.9 °C was interpreted as showing

$$B_2H_6 + \{B_4H_8\} \longrightarrow B_5H_{11} + \{BH_3\} \qquad (4)$$

that the loss of H_2 from B_4H_{10} was the rate-determining step (1) followed by reaction (4) to give B_5H_{11} and

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† Throughout this paper: 1 mmHg ≡ 13.6 × 9.8 Pa.

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

$\{BH_3\}$.[10] Earlier workers had suggested that B_4H_{10} decomposed by two simultaneous first-order paths to $\{B_4H_8\}$ and $\{B_3H_7\}$ species, the route to the latter being the rate-controlling step.[11] The arguments in favour of (1) and (4) as the major reactions giving B_5H_{11} compared to a route *via* $\{B_3H_7\}$ formed directly from B_4H_{10} include evidence that $\{B_3H_7\}$ and B_2H_6 react rapidly to give B_4H_{10},[10,12] and mass spectrometric confirmation of $\{B_4H_8\}$ but not $\{B_3H_7\}$ or $\{BH_3\}$ as species in the thermolysis of B_4H_{10}.[2,4,8a] Convincing as this may seem, we cannot completely rule out other, probably less important, routes to B_5H_{11} by reactions of B_4H_{10} with $\{BH_3\}$, $\{B_3H_7\}$, or even $\{B_4H_8\}$, reaction (5). Under our

$$\{B_4H_8\} + B_4H_{10} \longrightarrow B_5H_{11} + \{B_3H_7\} \qquad (5)$$

conditions it seems unlikely that reactions of B_2H_6 alone would be important sources of $\{BH_3\}$ and $\{B_3H_7\}$.[1]

It is possible that the B_6H_{10} observed originates by reaction (6), and B_6H_{12} by reaction (7). If reactions

$$2\{B_4H_8\} \longrightarrow B_2H_6 + B_6H_{10} \qquad (6)$$

$$\{B_4H_8\} + B_2H_6 \longrightarrow B_6H_{12} + H_2 \qquad (7)$$

such as (4), and less importantly (7), were significant then it would be expected that the concentration of B_6H_{10} would be lower than from a thermolysis of B_4H_{10} alone since B_2H_6 is competing for $\{B_4H_8\}$. If this were so then the concentration of $B_{10}H_{14}$ would also be lower (as observed) since B_6H_{10} is generally thought to be an intermediate along with B_9H_{15} and B_8H_{12} in the formation of $B_{10}H_{14}$.[6] A lack of $\{B_3H_7\}$ would also act to inhibit production of $B_{10}H_{14}$.

Cothermolysis of B_5H_9 *and* B_4H_{10} *at* 75 °C.—As far as the formation of products is concerned this reaction is very similar to the thermolysis of B_4H_{10} alone, B_5H_9 being unreactive when thermolysed at 75 °C.[1] A Figure deposited in SUP 22542 shows the variation of product concentration with time. The major product is B_5H_{11} with B_2H_6, $B_{10}H_{14}$, and hexaboranes (B_6H_{10} and B_6H_{12} in the ratio 2 : 3) also present. A slight reduction in B_5H_9 concentration was observed with small increases in the concentrations of B_2H_6 and $B_{10}H_{14}$ after 120 min compared to the thermolysis of B_4H_{10} alone. Reactions such as (8) and (9), followed by conversion of B_6H_{10} into $B_{10}H_{14}$, may account for these findings.

$$\{B_4H_8\} + B_5H_9 \longrightarrow \{B_3H_7\} + B_6H_{10} \qquad (8)$$

$$\{B_3H_7\} + B_5H_9 \longrightarrow B_2H_6 + B_6H_{10} \qquad (9)$$

The reaction of $\{BH_3\}$ and B_5H_9 at *ca.* 450 °C has been reported to produce a hexaborane but the hydrogen content was not ascertained.[13]

Attempted Cothermolysis of B_5H_{11} *and* B_4H_{10} *at* 75 °C.—The method used for the preparation of B_6H_{12} resulted in the isolation of a small amount of B_5H_{11} contaminated with B_6H_{12} (*ca.* 20% of the B_5H_{11} concentration). The B_5H_{11} so obtained could not be further purified and was used in the cothermolysis with B_4H_{10}; the results of this preliminary study (Figure 1) may therefore be less reliable than those of the other cothermolyses reported here, although it was established that the concentration of B_6H_{10} was zero at the start of the reaction.

With the thermolysis of B_4H_{10} itself producing B_5H_{11}, the concentration of B_5H_{11} increased during the first 45 min and thereafter decreased. This is in accord with the previous observations that B_4H_{10} is more reactive than B_5H_{11} and that B_5H_{11} is the major product from the thermolysis of B_4H_{10}.[1] Of the other products, both B_2H_6 and $B_{10}H_{14}$ were formed in larger amounts after 120 min than would have been expected from equivalent amounts of B_4H_{10}, B_5H_{11}, and B_6H_{12} thermolysed separately. This can be attributed to the increased importance of reaction (6) with an increased concentration of $\{B_4H_8\}$ being supplied *via* reaction (10).

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

The B_6H_{10} would be subsequently converted into $B_{10}H_{14}$. The concentration of hexaboranes increases during the first 45 min of reaction and then decreases. After 120 min the ratio of B_6H_{10} to B_6H_{12} is *ca.* 1 : 1.

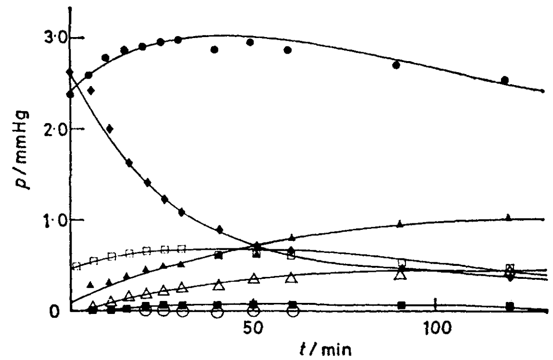

FIGURE 1 Cothermolysis of B_4H_{10} and B_5H_{11} at 75 °C. Boranes: B_4H_{10} (♦), B_5H_{11} (●), B_6H_{10}–B_6H_{12} (□), B_2H_6 (▲), $B_{10}H_{14}$ (△), B_8H_{12} (■), B_9H_{15} (○)

Cothermolysis of B_6H_{10} *and* B_4H_{10} *at* 75 °C.—With B_4H_{10} present the initial concentration of B_6H_{10} was reduced by 86% in 120 min. Thermolysis of B_6H_{10} alone showed a reduction of *ca.* 9% in 120 min.[1] The cothermolysis (Figure 2) produced B_5H_{11}, B_2H_6, and $B_{10}H_{14}$ as major products and a small amount of B_5H_9 after 120 min. Substantial concentrations of B_8H_{12} and B_9H_{15} built up over the first 30—40 min and then decreased. At the end of the reaction time the ratio of B_6H_{10} to B_6H_{12} present was 3 : 1. The increased proportions of B_2H_6, B_8H_{12}, B_9H_{15}, and $B_{10}H_{14}$ observed can be explained simply by reactions (11)—(13), or by more

$$\{B_4H_8\} + B_6H_{10} \longrightarrow B_9H_{15} + \{BH_3\} \qquad (11)$$

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

$$B_8H_{12} + \{B_4H_8\} \longrightarrow B_{10}H_{14} + B_2H_6 \qquad (13)$$

complicated routes, *e.g.* those involving $\{B_9H_{13}\}$ and $\{B_3H_7\}$ as proposed by Long[6] in the thermolysis of B_2H_6. There is good evidence for reactions (11)[14] and (12),[8b] but (13) has not been studied separately.

As well as in (13), B_2H_6 would be produced *via* reaction (6). The observation of relatively small amounts of B_6H_{12} and B_5H_9 (*ca.* 10% of pentaboranes at $t = 120$ min) can be explained in terms of reaction (7) giving B_6H_{12} which then either decomposes by (14) or reacts with $\{B_4H_8\}$, reaction (15).

$$B_6H_{12} \longrightarrow B_5H_9 + \{BH_3\} \qquad (14)$$

$$\{B_4H_8\} + B_6H_{12} \longrightarrow B_5H_9 + B_5H_{11} \qquad (15)$$

Cothermolysis of B_6H_{12} *and* B_4H_{10} *at* 75 °C (*Figure* 3).—The rate of decomposition of B_6H_{12} in cothermolysis with B_4H_{10} appeared to be slower than B_6H_{12} alone. This was due to the formation of B_6H_{10} from B_4H_{10},[1] producing a mixture of B_6H_{12} and B_6H_{10}. After 120 min the ratio of B_6H_{10} to B_6H_{12} was 1 : 3.

Greater concentrations of B_2H_6 and $B_{10}H_{14}$ were observed after 120 min than would have been expected from separate thermolyses of B_4H_{10} and B_6H_{12}. A mixture of pentaboranes B_5H_9 and B_5H_{11} in the ratio 2 : 3 was found after 120 min. To understand these observations one can postulate that the important reactions in the cothermolysis are (14) and (15) giving B_5H_9 and B_5H_{11}, (10) and (1) giving $\{B_4H_8\}$, (6) giving B_6H_{10}, and (11)—(13) producing $B_{10}H_{14}$. Reaction (8) could play a part in B_6H_{10} formation and other reactions involving $\{B_3H_7\}$ may occur to some extent.

In conclusion, we have shown that the recently developed method of analysis of mixtures of boranes based on mass spectrometry provides consistent results on the cothermolysis of boranes, which can be interpreted in a self-consistent manner. Comparison of these results with data from the thermolysis of individual boranes is a very useful approach to the complex problem of understanding the thermolytic interconversion reactions of boranes. In particular, it now appears that $\{B_4H_8\}$ is a reactive intermediate of major importance in reactions of B_4H_{10} with B_2H_6, B_5H_9, B_5H_{11}, B_6H_{10}, and B_6H_{12}, and that B_6H_{10} is the most important stable borane precursor for the efficient production of $B_{10}H_{14}$ under the experimental conditions used.

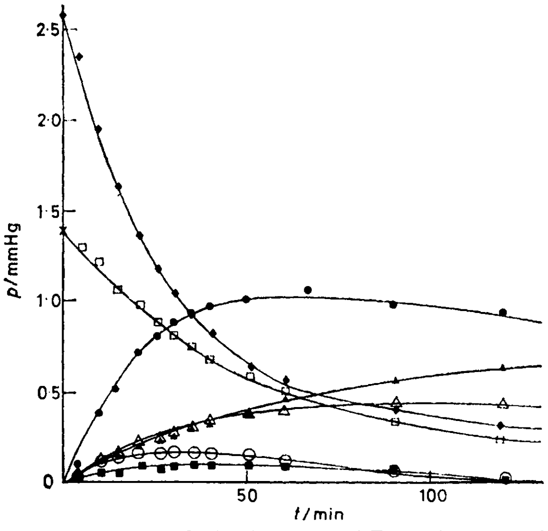

FIGURE 2 Cothermolysis of B_4H_{10} and B_6H_{10} (×) at 75 °C. Boranes as in Figure 1

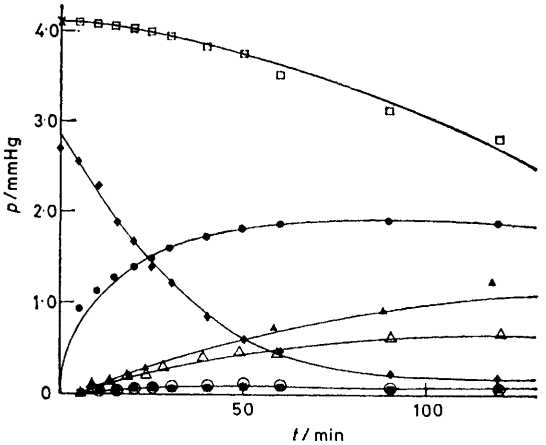

FIGURE 3 Cothermolysis of B_4H_{10} and B_6H_{12} (×) at 75 °C. Boranes as in Figure 1

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