Kinetics and Mechanism of the Thermal Decomposition of Hexaborane(12) in the Gas Phase

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The gas-phase thermolysis of *arachno*-B_6H_{12} produces 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}; these results imply a mechanism involving elimination of BH_3 as the rate-determining initial step in both reactions.

Progress has been slow in elucidating a coherent mechanistic description of the facile thermal interconversions of the simple binary boranes, not only because of the inherent complexity of the reactions but also because of difficulties in acquiring reliable kinetic data for these highly reactive, air-sensitive species.[1] We have developed a quantitative mass spectrometric technique for monitoring these reactions in detail, and have thereby gained new insights into the thermal decompositions and interconversion reactions of *nido*-B_6H_{10}[2] and the two *arachno* species B_4H_{10}[3,4a] and B_5H_{11}.[4] We now report preliminary results of the first quantitative kinetic study on B_6H_{12}. The results are important because they provide the first opportunity to correlate kinetic, mechanistic, and structural patterns of behaviour in a unique series of closely related *arachno* binary boranes.

A typical reaction profile for the thermolysis of B_6H_{12} at *ca.* 100 °C is shown in Figure 1 for an initial pressure of 3.14 mmHg. From this and similar profiles recorded over the pressure and temperature ranges 1.8—10.0 mmHg and 75—150 °C, it emerges that this thermolysis is the most straightforward of all borane decompositions studied so far. The overall stoicheiometry is very well defined, with at least 80% of the B_6H_{12} decomposing to B_5H_9 plus $\frac{1}{2}B_2H_6$. From a detailed analysis of initial rates, the consumption of B_6H_{12} and the production of B_5H_9 and of B_2H_6 were all found to be accurately first-order with respect to the concentration of B_6H_{12}. In addition, a small amount of H_2 is produced, and even less B_6H_{10}; the latter builds up rather slowly but persists in the later stages of the reaction when all the B_6H_{12} has decomposed. Only traces of higher boranes such as $B_{10}H_{14}$ are observed, and involatile solid hydrides account for as little as 10% of the boron consumed, compared with typical values of 40—50% in the thermolysis of B_4H_{10}[3] and B_5H_{11}.[4b]

These results can readily be explained by a simple two-step mechanism involving the first order rate-determining elimination of $\{BH_3\}$ which then rapidly dimerizes to B_2H_6 [reactions (1) and (2)]. Previous qualitative studies of the decomposition of B_6H_{12} in the gas phase[5] have yielded no mechanistic information and have sometimes suggested more complex behaviour than observed in the present work.

$$B_6H_{12} \xrightarrow{\text{slow}} B_5H_9 + \{BH_3\} \quad (1)$$

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

$$B_5H_{11} \rightarrow \{B_4H_8\} + \{BH_3\} \quad (3)$$

Our recent kinetic study of B_5H_{11}[4] has shown that this borane also decomposes *via* the initial rate-determining elimination of $\{BH_3\}$ from the cluster [reaction (3)], and it is therefore particularly significant that the activation energy and pre-exponential factor now found for the B_6H_{12} thermolysis (E_a 75.0 ± 5.8 kJ mol^{-1}; A 3.8 × 10^7 s^{-1}) are essentially identical to the values obtained for B_5H_{11} (E_a 72.6 ± 2.4 kJ mol^{-1}; A 1.3 × 10^7 s^{-1}). This is persuasive additional evidence that the rate-determining steps in the two decompositions do indeed involve very similar processes and this finds a ready interpretation in terms of the detailed molecular structures of gaseous B_5H_{11}[6] and B_6H_{12},[7] as recently determined by electron diffraction. As shown in Figure 2,[7] these two species bear a close structural relationship to each other and to B_4H_{10}.[8] Thus, notional replacement of H_{endo} and one H_μ on, say, B(4) in B_4H_{10} by a BH_3 group yields B_5H_{11} and

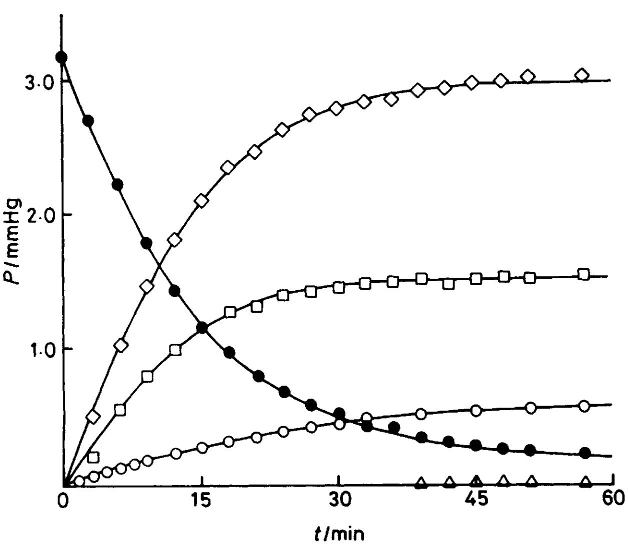

Figure 1. Reaction profile for the thermolysis of B_6H_{12} (P_0 3.14 mmHg) at 99.4 °C. ● B_6H_{12}, ◇ B_5H_9, □ B_2H_6, △ $B_{10}H_{14}$, and ○ H_2.

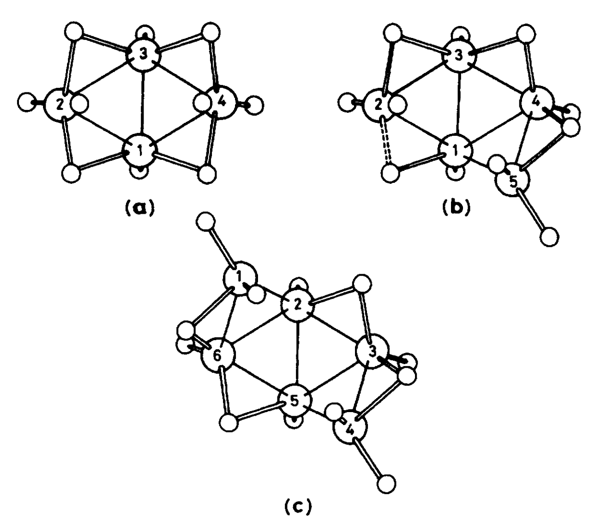

Figure 2. Structural relationship between the *arachno*-boranes (a) B_4H_{10},[8] (b) B_5H_{11},[6] and (c) B_6H_{12},[7] as determined by gas-phase electron diffraction.

repetition of this process on the opposite side of the molecule, *i.e.* at B(2), generates the observed structure of B_6H_{12} having C_2 symmetry. In view of the similarity of the Arrhenius parameters for the decomposition of B_6H_{12} and B_5H_{11}, it seems reasonable to identify these structurally similar BH_3 groups as the fragments involved in the initial steps (1) and (3). In B_4H_{10}, by contrast, these particular incipient BH_3 groups are absent and its decomposition is characterized by quite different Arrhenius parameters (E_a 99.2 ± 0.8 kJ mol^{-1}; A 6.0 × 10^{11} s^{-1}).[3] In this case the initial step is believed to involve elimination of H_2 to give $\{B_4H_8\}$. This type of reaction is clearly not favoured in the case of B_5H_{11} and B_6H_{12}, though small amounts of B_6H_{10} are produced in the thermolysis of B_6H_{12}, and further work is necessary to determine whether this species and dihydrogen arise from a competing, but minor, reaction channel involving direct elimination of H_2 from B_6H_{12}.

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