

UV LASER PHOTOCHEMISTRY OF PENTABORANE(9) AT 193 nm: QUANTUM YIELD OF PRIMARY BH₃ FORMATION AND ITS SUBSEQUENT CHEMISTRY

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Summary

Excitation of B₅H₉ in the gas phase by ArF laser radiation at 193 nm causes primary dissociation into BH₃ plus B₄H₆. Rapid recombination probably leads to the reactive intermediate B₅H₇, which upon addition to B₅H₉ forms B₁₀H₁₄ and B₁₀H₁₆. B₆H₁₀ production as well as polymerization can be understood to proceed via the intermediate B₈H₁₂, which arises from the dimerization of B₄H₆ fragments.

1. Introduction

Measurement of the quantum yield of primary BH₃ production from ArF laser-excited B₂H₆ [1] and the UV absorption of gaseous B₅H₉ [2] has led to interest in the primary step in B₅H₉ photolysis. Apart from an early article on the irradiation of pentaborane(9) vapour [3] and some mercury sensitization work [4, 5], very little information is available in the literature on the photochemistry of B₅H₉.

Generally, the main products of B₅H₉ photolysis are hydrogen, diborane(6), decaborane(14) and decaborane(16). For direct excitation [3], Hg(³P₁) sensitization [4], glow discharge [6] and radiation-chemical experiments [7], there seems to be agreement on the radical B₅H₈· as the reactive intermediate, originating from the primary step



Decaborane formation is thought to proceed through recombination, followed in part by an H₂ elimination:



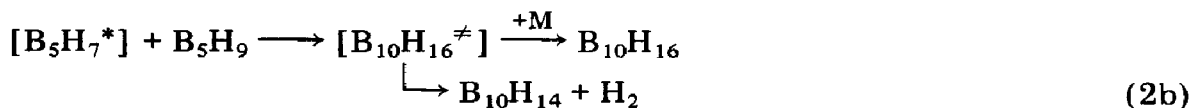
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Kline and Porter were the first workers to give results which deviate from this scheme [5]. Using results from isotope studies, they proposed the existence of the previously unknown neutral intermediate B_5H_7 .

In $Hg(^3P_1)$ sensitization, the fragment $[B_5H_7^*]$ could be generated in the primary step:



Collision of the intermediate $[B_5H_7^*]$ with a thermal B_5H_9 molecule would be sufficient to form stable products:



The existence of the free radical $B_5H_8\cdot$ appears doubtful.

This work deals with ArF laser excitation of gaseous B_5H_9 at 193 nm. The nature and quantum yield of the primary step were determined and possible subsequent reactions are discussed. Additional evidence for decaborane production via the reactive intermediate B_5H_7 will be presented.

2. Experimental details

The quantum yield of BH_3 from optically excited $B_5H_9^*$ was measured by the same method as in the case of $B_2H_6^*$ [1]. Pentaborane(9), together with various amounts of PF_3 , was filled into a glass cell (105 mm long, 34 mm in diameter) equipped with a pair of Suprasil windows and a pair of KBr windows in the perpendicular position. The primary product from ArF laser photolysis was trapped by fast addition reaction to PF_3 . The resulting adduct was then monitored by its IR absorption with a Beckman IR-12A grating spectrometer.

The beam of a Lambda-Physik EMG-102 exciplex laser was expanded to fill most of the cell volume and its energy density was limited to less than 10 mJ cm^{-2} , excluding heating as well as multiphoton effects. In order to ensure the same conditions for all samples, such as UV absorption strength and subsequent chemistry, the initial B_5H_9 pressure was held constant at about 0.5 Torr. In the case of pure pentaborane samples, the pressure was varied between 0.5 and 5.0 Torr. Individual samples were only irradiated up to a maximum extent of about 20% reaction to avoid non-linearity. Thermal reaction between B_5H_9 and PF_3 was found to be sufficiently slow so as not to play an important role. A grease-free high vacuum line was employed to handle the pentaborane(9), which had been obtained from Callery Chemical Co. Before use, this compound was subjected to trap-to-trap distillation, until its mass spectrum, taken on a Bendix TOF mass analyser, and its IR spectrum revealed that no impurities were present. PF_3 was delivered by Fluorochem and was purified in the laboratory by the method described previously.

3. Results and discussion

3.1. Primary process in B_5H_9 photolysis at 193 nm

Irradiation of gaseous B_5H_9 - PF_3 mixtures with ArF laser pulses leads to the formation of the stable adduct $BH_3 \cdot PF_3$. In complete analogy to the procedure for B_2H_6 [1], the amount of $BH_3 \cdot PF_3$ was followed by its IR absorption at 943 cm^{-1} (absorption coefficient (base e), $0.117\text{ cm}^{-1}\text{ Torr}^{-1}$ [8]), and was taken as a measure for primary BH_3 production. The so-determined BH_3 quantum yields Φ_{BH_3} , as a function of PF_3 excess are displayed in Fig. 1. As the excess of PF_3 is increased, the Φ_{BH_3} are seen to approach the limiting value of 1.0 ± 0.1 , which they finally reach only at an excess of 70:1 or greater.

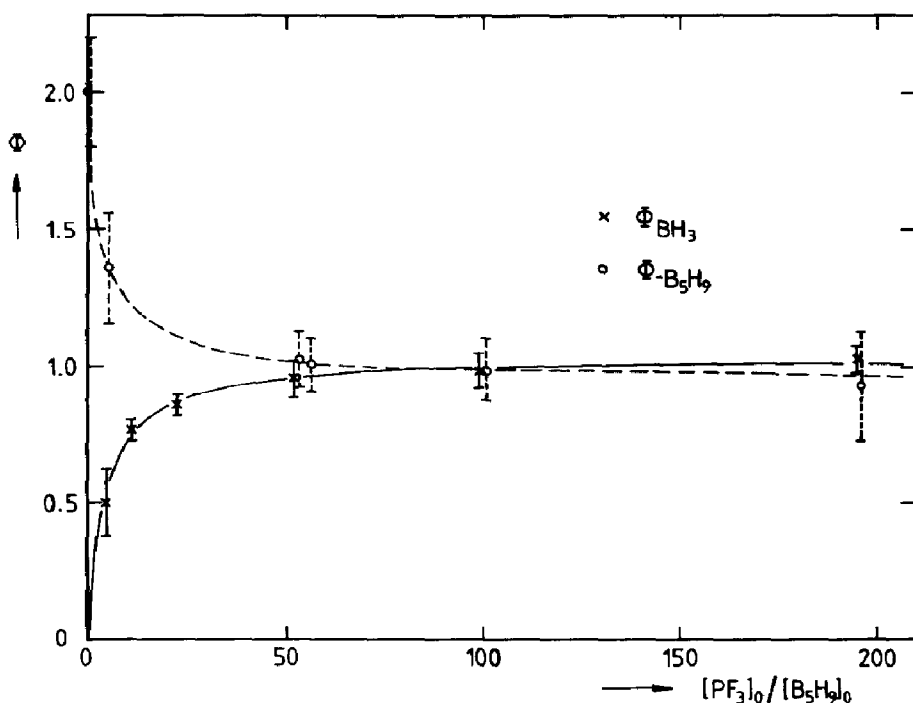


Fig. 1. Quantum yields Φ_{BH_3} and $\Phi_{-B_5H_9}$, of BH_3 production and B_5H_9 disappearance from ArF laser photolysis of various B_5H_9 - PF_3 mixtures as a function of initial pressure ratios.

This allows us to formulate the primary process as follows:



and to conclude that any subsequent reactions of BH_3 , such as



must be very fast, compared with the trapping reaction



whose rate constant k_5 was determined to be $1.5 \times 10^8 \text{ l mol}^{-1} \text{ cm}^{-1}$ [9].

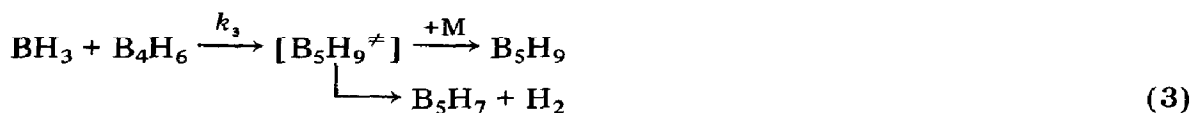
3.2. Chemistry subsequent to the excitation of B_5H_9 at 193 nm

When pentaborane(9) was irradiated for a longer period of time at a pressure of about 5 Torr, with or without PF_3 , a colourless solid always appeared on the cell walls and windows. The gas phase mass spectra, however, did not indicate that any higher boranes had been formed.

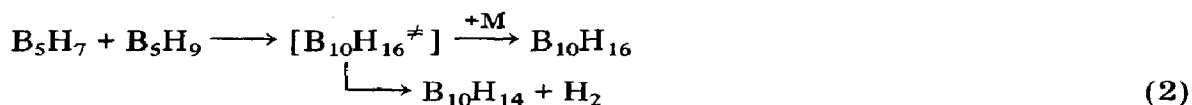
As the solid product apparently had an extremely low vapour pressure, any volatile compounds were pumped off and the variable leak valve of the inlet system was opened wide. This led to the appearance of new features in the mass spectra. In the case of B_5H_9 irradiated without PF_3 , B_6H_{10} was now observed, together with $\text{B}_{10}\text{H}_{14}$ and $\text{B}_{10}\text{H}_{16}$ in even higher quantities. In the case of irradiated B_5H_9 - PF_3 mixtures, B_6H_{10} had been formed in similar amounts, but it was hard to detect any decaborane at all. As the colourless solid was present in both cases, but the decaboranes only in one case, this solid cannot be identified as any one of them. It is therefore assumed to consist mainly of a borohydride polymer $(\text{B}_2\text{H}_2)_n$ with some B_6H_{10} adsorbed on its surface.

Figure 1 also shows the quantum yields $\Phi_{-\text{B}_5\text{H}_9}$ of B_5H_9 disappearance as determined by the IR absorption at 2610 cm^{-1} [10] (absorption coefficient, $0.025 \text{ cm}^{-1} \text{ Torr}^{-1}$ according to our own measurement). For samples of pure B_5H_9 , this quantum yield is pressure dependent and reaches a limiting value of 2.0 ± 0.2 from about 2 Torr upwards. On increasing the excess of PF_3 , the quantum yield falls until it ultimately approaches the value of 0.9 ± 0.2 (probably 1.0 with better accuracy).

Taking all these experimental observations into account, the following reactions are proposed to occur after the excitation at 193 nm:

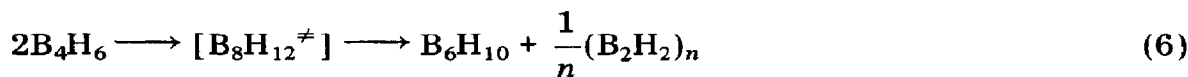


Decaborane formation may be explained via



in accordance with ref. 5, as mentioned above.

Traces of hexaborane(10), together with a borohydride polymer $(\text{B}_2\text{H}_2)_n$, may originate from the dimerization of B_4H_6 fragments via the reactive intermediate $[\text{B}_8\text{H}_{12}]$, which is known to yield B_6H_{10} in a first-order decomposition reaction [11]:

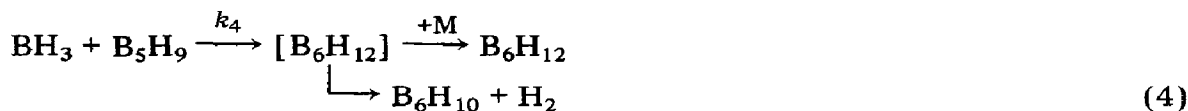


To some extent, the intermediates may polymerize as well:



This will take place unless there is enough of another borohydride present, with which they react faster.

The reaction of BH_3 with B_4H_6 (reaction (3)) can be safely assumed to occur extremely fast compared with the competing reaction with B_5H_9 :



For example, in the case of a PF_3 -to- B_5H_9 pressure ratio of 5, only about half of the total BH_3 formed in the primary step (1) is trapped by PF_3 , whereas more than one B_5H_9 molecule decomposes per photon absorbed ($\Phi_{\text{BH}_3} = 0.5$; $\Phi_{-\text{B}_5\text{H}_9} = 1.35$; Fig. 1). The ratio of primary BH_3 , B_4H_6 , B_5H_9 and PF_3 concentrations is approximately 1:1:300:1000. The rate constant for BH_3 plus B_5H_9 (reaction (4)) was estimated to be $10^7 \text{ l mol}^{-1} \text{ cm}^{-1}$ [12], and that for BH_3 plus PF_3 (reaction (5)) is given as $1.5 \times 10^8 \text{ l mol}^{-1} \text{ cm}^{-1}$ [9]. Therefore, the chance of reaction (4) competing with reaction (5) is less than 1 in 50. Most of the BH_3 that has managed to escape being trapped by PF_3 (reaction (5)) thus takes part in the very fast reaction with B_4H_6 (reaction (3)), where $k_3 \approx 10^3 k_5 = 10^{11} \text{ l mol}^{-1} \text{ cm}^{-1}$ (rough estimate). From the preceding discussion, it may be concluded that hexaborane formation via route (4) will be negligible in our case.

When PF_3 is added in higher excess, the primarily generated BH_3 is almost completely consumed in adduct formation (reaction (1)). Reactions (3) and (2) are suppressed and decaborane is no longer produced. Hexaborane(10), however, may still arise as in the case of pure B_5H_9 , for dimerization of B_4H_6 with successive decomposition (reaction (6)) is not hindered at all.

On increasing the excess of PF_3 over B_5H_9 , the quantum yield of B_5H_9 disappearance should eventually approach unity as no more than one molecule of pentaborane(9) should be destroyed (by photodissociation in the primary step) per photon absorbed. However, when B_5H_9 is irradiated pure, two molecules should be lost per photon absorbed; in this case, one more borohydride molecule would be taken up in the chemistry subsequent to excitation and so the quantum yield of B_5H_9 disappearance should change to 2.0. The proposed mechanism can explain experimental observations very well indeed and even support recent findings [5].

In order to evaluate the suggested routes of decaborane formation, let us briefly summarize what is known about thermal reactions. Generally,

B_5H_9 seems to be a necessary precursor of $B_{10}H_{14}$, but the mechanism is not clear.

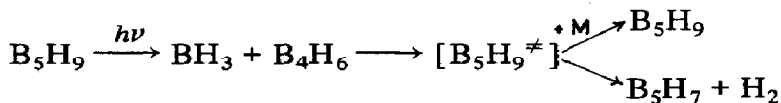
IR laser excitation of B_2H_6 at 973 cm^{-1} [13 - 15] produces H_2 , B_5H_9 , B_5H_{11} , $B_{10}H_{14}$, $(B_2H_2)_n$ [13, 14] and sometimes $B_{20}H_{16}$ [15]. Addition of B_5H_9 before irradiation will enhance the $B_{10}H_{14}$ quantum yield [14]. No mechanism is discussed in the quoted literature, however.

The pyrolysis of pure B_5H_9 gives a non-volatile solid as the main product [16]. In contrast, the copyrolysis of B_2H_6 and B_5H_9 yields mainly $B_{10}H_{14}$, suggesting that five of the boron atoms in $B_{10}H_{14}$ come from B_2H_6 [17]. This justifies the conclusion of a stepwise build-up of decaborane(14) from pentaborane(9) through higher boranes. A major problem with this hypothesis is, however, that one step in the build-up sequence is missing: no heptaborane has ever been detected unequivocally [11, 16]. Even in a more recent investigation [18] no detailed mechanism is discussed. Decaborane may be formed through B_9H_{15} or B_8H_{12} , originating from the reaction of B_5H_9 with the intermediates of B_2H_6 pyrolysis, such as B_3H_7 or B_4H_8 [16, 18]. These fragments may play an important role under static conditions as in the copyrolysis of borane mixtures, but need not be considered in the case of photolysis of pure pentaborane, as performed in our experiment.

The proposed mechanism may also serve to explain thermal decaborane formation more clearly.

4. Conclusion

Direct photolysis of pentaborane(9) in the gas phase at 193 nm provides evidence for the primary process



where addition of the neutral fragment B_5H_7 to a B_5H_9 molecule leads to decaborane formation. Hexaborane(10), together with a polymer, is probably produced by decomposition of B_8H_{12} from the dimerization of B_4H_6 reactive intermediates.

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