

UV LASER PHOTOCHEMISTRY OF DIBORANE AT 193 nm: QUANTUM YIELD FOR BH₃ PRODUCTION

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Summary

The quantum yield ϕ_{BH_3} for BH₃ production from ArF-laser-excited B₂H₆ was determined to be 2.00 ± 0.25 by trapping with PF₃. The former postulate of BH₃ as a chain carrier in ArF-laser-induced B₂H₆-D₂ exchange is confirmed.

1. Introduction

In our previous paper [1], we reported that the ArF-laser-induced deuteration of B₂H₆ proceeds via a chain reaction, with BH₃ as a chain carrier. The observed fast exchange of the irradiated B₂H₆ with D₂ was most favourably explained by the elementary step



together with the consecutive reactions of BH₂D. From the computer modelling of the final B₂H₅D concentrations as a function of the energy absorbed, there was evidence for the homogeneous dissociation



to be the dominant primary step in the UV laser photolysis of B₂H₆ at 193 nm.

In the current literature, however, the heterogeneous dissociation

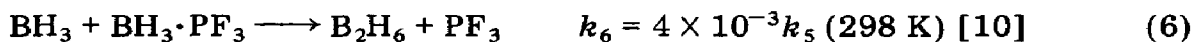
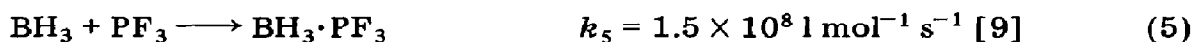
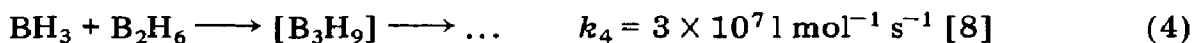
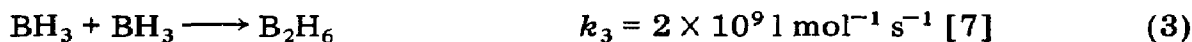


is generally accepted as the main primary step of B₂H₆ photolysis [2 - 5], although the B₂H₅[·] radical as such has never been seen. Therefore, more direct proof of the dominant reaction (2a) is desirable.

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As the physical detection of a short-lived highly reactive intermediate such as BH_3 imposes serious problems, chemical trapping was used in this study. In principle, the electron-donating ligands CO and PF_3 are well suited as trapping agents for the electron-deficient BH_3 . They both form an adduct in a very fast reaction. $\text{BH}_3 \cdot \text{CO}$, however, shows a much stronger absorption at 193 nm than B_2H_6 itself [6], and therefore is ruled out in this case.

If the competing reactions



of BH_3 , whose rate constants have been determined, are considered it becomes apparent that even at a moderate excess of PF_3 over B_2H_6 the trapping reaction (5) should be strongly preferred to reactions (3), (4) and (6).

2. Experimental details

In a glass cell, 105 mm in length and 35 mm in diameter, mixtures of B_2H_6 and PF_3 were prepared and irradiated using an ArF laser. The cell was equipped with a pair of Suprasil windows and a pair of KBr windows, perpendicular to each other, allowing IR spectra to be recorded immediately after UV irradiation. In order to avoid polymer formation from B_2H_6 , the rectangular (5 mm \times 25 mm) beam of a Lambda Physik model EMG-102 laser was expanded and a spherical portion about 20 mm in diameter was selected from it. The incident energy was limited to 30 mJ pulse⁻¹ so that the photon density did not exceed 10 mJ cm⁻². The laser was operated at a repetition rate of about 0.5 Hz.

The amount of $\text{BH}_3 \cdot \text{PF}_3$ generated was measured by employing quantitative IR absorption spectroscopy, using a Beckman type IR-12A grating spectrometer. Chien and Bauer [11] reported the extinction coefficient of this compound at 943 cm⁻¹ (its most intense absorption band [12]) as 0.117 cm⁻¹ Torr⁻¹. Fortunately, this band fits exactly between one band of B_2H_6 and another of PF_3 , permitting the measurement of low BH_3PF_3 concentrations in the presence of high B_2H_6 or PF_3 contents.

The whole experimental procedure could be carried out sufficiently quickly that it was unnecessary to correct for the thermal reaction between B_2H_6 and PF_3 , which proved to be fairly slow for the pressures employed.

The diborane was prepared according to standard methods [13] at the Institut für Anorganische Chemie der Universität München. Phosphorous trifluoride of unspecified purity was delivered by Fluorochem (Gt. Britain). It was found to contain considerable amounts of HCl and HF and therefore exhibited strong absorption at 193 nm, while pure PF_3 should not absorb at

TABLE 1

Experimental quantum yields ϕ_{BH_3} for BH_3 production from ArF-laser-excited B_2H_6

n^0	$P^0_{\text{B}_2\text{H}_6}$	$P^0_{\text{PF}_3}/P^0_{\text{B}_2\text{H}_6}$	ϕ_{BH_3}
1	7.0	1.4	2.09 ± 0.17
2	7.1	6.0	1.83 ± 0.20
3	7.1	10.1	2.04 ± 0.21
4	7.1	15.2	1.85 ± 0.16
5	7.2	18.9	2.10 ± 0.18

$P^0_{\text{B}_2\text{H}_6}$, initial partial pressure of B_2H_6 in torr; $P^0_{\text{PF}_3}$, initial partial pressure of PF_3 in torr.

wavelengths longer than 160 nm [14]. Thus the sample was purified by bubbling the gas sequentially through tri-*N*-butylamine and concentrated sulphuric acid and drying with phosphorous pentoxide.

3. Results and discussion

Table 1 shows the BH_3 quantum yields of B_2H_6 determined in the above-described way for several runs under different experimental conditions.

Whereas the B_2H_6 partial pressure is kept almost constant, the excess of PF_3 is varied by a factor of about 20. However, as was anticipated with reference to reactions (3) - (6), this change did not affect the BH_3 quantum yields. The trapping reaction (5) is always fast enough to convert all BH_3 to $\text{BH}_3 \cdot \text{PF}_3$.

Within the range of experimental error, the quantum yield ϕ_{BH_3} for BH_3 formation by photodissociation of B_2H_6 at 193 nm is determined to be 2.00 ± 0.25 .

For one molecule excited two BH_3 fragments are formed and the efficiency of the heterogeneous dissociation to $\text{B}_2\text{H}_5^\cdot + \text{H}^\cdot$ (reaction (2b)) must indeed be very low. This implies also that the B_2H_6 molecule is not de-excited by collisions with ground state B_2H_6 , or added foreign molecules such as PF_3 , before dissociation occurs. In this way, our previous postulate in ref. 1 is affirmed. An additional experiment serves to confirm this result. If B_2H_6 is photolysed in a tenfold excess of D_2 and a 20-fold excess of PF_3 , again only $\text{BH}_3 \cdot \text{PF}_3$ is formed with a quantum yield of about 2.0.

4. Conclusion

We have demonstrated that the homogeneous primary step (2a), $\text{B}_2\text{H}_6 + h\nu \rightarrow 2\text{BH}_3$, plays the dominant role in the UV laser photolysis of B_2H_6 at 193 nm. The contribution from the alternative heterogeneous dissociation (2b) turns out to be negligible.

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