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CO_2-Laser-Driven Reactions of B_2H_6 and B_2H_6/B_5H_9 Mixtures[1]

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Irradiation of neat B_2H_6 and B_2H_6/B_5H_9 mixtures with the output from a CW CO_2 laser operating on the R(16) line of the 10.6-μm transition (973.3 cm^{-1}) induces an apparent thermal reaction in which $B_{10}H_{14}$ is produced. Greater than 65% of the starting material that undergoes reaction is converted to $B_{10}H_{14}$ under certain experimental conditions. Furthermore, less than 1400 photons are required to produce each $B_{10}H_{14}$ molecule when B_2H_6/B_5H_9 mixtures are irradiated.

1. Introduction

The pyrolysis of diborane (B_2H_6) has long been used as a method for the production of higher boranes.[2-4] In particular, tetraborane (B_4H_{10}), pentaboranes (both B_5H_9 and B_5H_{11}), and decaborane ($B_{10}H_{14}$) are obtained as the primary products upon thermal decomposition of B_2H_6. An undesirable, nonvolatile, solid hydride is also generally formed upon pyrolysis of B_2H_6. Studies of the copyrolysis of B_2H_6 and B_5H_9 have indicated that decaborane is formed as the principal product.[5,6] Furthermoe, this reaction occurs at temperatures where B_5H_9 is stable,[3] suggesting the reaction proceeds via fragments generated by decomposition of the diborane.

In the last several years a number of reports[7-9] have appeared in which a CW CO_2 laser tuned to an infrared absorption feature in B_2H_6 resulted in the production of higher boranes. Bachmann et al.[7] reported that irradiation of B_2H_6 produced predominantly icosaborane ($B_{20}H_{16}$) with a concomitant visible luminescence. These investigators invoked a laser-initiated chain reaction to explain the high product yield. More recent studies of the CW CO_2-laser-driven reaction of B_2H_6 failed to reproduce these result.[8,9] In fact, the products observed were H_2, B_5H_9, B_5H_{11}, $B_{10}H_{14}$, and a boron hydride polymer. Additionally, a very large number of photons was required to produce the various boranes (22 000 for each $B_{10}H_{14}$ molecule), an observation apparently inconsistent with a chain mechanism.

Considering the discrepancies among earlier reports and the importance of $B_{10}H_{14}$ in the synthesis of icosahedral carboranes,[10] it was felt that a reinvestigation of the CO_2-laser-driven reactions of B_2H_6 was worthwhile. The purpose was to determine the products formed and to optimize the yield of $B_{10}H_{14}$ (reported as 5–13% in ref 9), while at the same time the number of photons required to produce this species was reduced. Furthermore, since copyrolysis of B_2H_6 and B_5H_9 results in efficient production of $B_{10}H_{14}$, CO_2-laser irradiation of mixtures of these materials was investigated as an alternative to laser-stimulated reaction of neat diborane. Extremely promising results were obtained with these mixtures. Yields of $B_{10}H_{14}$ in excess of 65% were obtained, and photon requirements were reduced to less than 1400 per $B_{10}H_{14}$ molecule.

2. Experimental Section

Diborane was obtained from Matheson Gas Co. at a concentration of 1.1% in helium. B_2H_6 was separated from He by introducing 500 torr of the mixture into a metal, high-vacuum system to which a 1.1-L bulb equipped with a cold finger was attached. The cold finger was immersed in liquid nitrogen, freezing the B_2H_6 and allowing the helium to be pumped away. B_2H_6 was subsequently transferred to a storage vessel. Prior to use of B_2H_6, the cold finger on the storage bulb was immersed in an pentane slush (−130 °C) in order to condense any higher boranes which form slowly at ambient temperature.[4] Infrared spectra of the diborane obtained in this manner revealed no impurities. B_5H_9 was obtained from Callery Chemical Co. This material was further purified by passing it through a chlorobenzene slush (−45 °C) into a liquid-nitrogen trap. Again, an infrared spectrum revealed no impurity species.

For determination of the amounts of the individual volatile components generated via CO_2-laser irradiation of either B_2H_6 or B_2H_6/B_5H_9 mixtures, the volume of a portion of the vacuum manifold was calibrated. The volumes of the various reaction cells employed were also determined. Pressure measurement was accomplished with 3 MKS Baratron capacitance manometers attached to the calibrated section of the vacuum system. Pressures from 10^{-3} to 10^3 torr could be measured to an absolute accuracy of better than 0.2%. Separation of the individual volatile components was achieved by immersion of the reaction-cell cold finger in different low-temperature baths. The total pressure following irradiation was first determined by expansion into the calibrated volume. The reaction-cell cold finger was then immersed in liquid nitrogen which condensed all components except H_2. The hydrogen was then pumped away. The cold finger was then allowed to warm to ambient temperature, and the pressure in the calibrated volume was measured. The difference between this pressure and the pressure found immediately following irradiation yields the H_2 pressure. Repeating this procedure first with a pentane slush (−130 °C), followed by a chlorobenzene slush (−45 °C), allowed the pressures of the residual B_2H_6 and pentaboranes (B_5H_9 and B_5H_{11}) to be determined. At this point only $B_{10}H_{14}$ crystals and a boron hydride polymer remained in the cold finger. The $B_{10}H_{14}$ crystals were sublimed in vacuo to a preweighed sample tube immersed in liquid N_2. The weight was then determined gravimetrically. Any weight difference between the amount of material that underwent reaction and the total weight of H_2 and higher boranes formed was attributed to the yellow boron hydride polymer which remained on the reaction cell walls.

The reaction cells were made of Pyrex tubing and ranged from 40 to 50 mm in diameter. All cells were 10 cm long and were equipped with cold fingers. NaCl end windows were attached to the cells either by epoxy adhesive or by high-vacuum O-ring seals. The cells fit directly into the sample compartment of a Perkin-Elmer Model 599 infrared spectrophotometer. Infrared spectra could thus be conveniently recorded both prior to and following irradiation of B_2H_6 or B_2H_6/B_5H_9 mixtures, as well as during various phases of separating the volatile components generated.

An Advanced Kinetics Model MIRL-50 grating-tuned CO_2 laser was used to irradiate the gas samples. In all cases the laser was turned to the R(16) line of the 10.6-μm transition (973.3 cm^{-1}). This laser frequency is the same as that used by previous investigators.[7-9] Up to 25 W (~90 W/cm^2) of output power could be obtained on this line. Two power meters were used in conjunction with the laser. One monitored the power transmitted through the cell, while the other monitored a portion of the beam (16%) reflected from a beam splitter placed in front of the cell. The output from the power meters was

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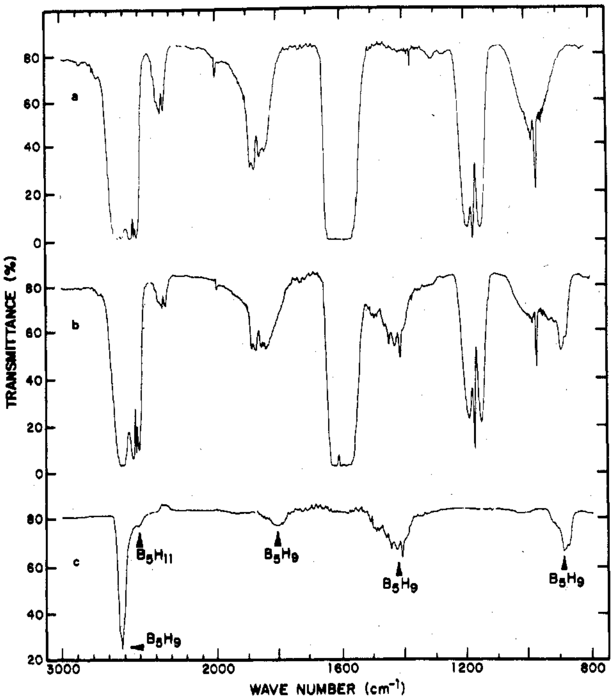

Figure 1. Spectrum of diborane (a) prior to irradiation, (b) immediately following irradiation with R(16) line of the 10.6 μm CO_2-laser transition, and (c) after removal of the unreacted B_2H_6 and the H_2 generated from the irradiated sample.

recorded on a dual-pen strip-chart recorder. The total amount of energy deposited in the sample could be calculated from the outputs of the two detectors. This energy, along with the amount of material formed, was used to compute quantum yields.

3. Results and Discussion

Initially, samples of neat diborane were irradiated in a cell having an inside diameter of 42 mm and a volume of 167.8 cm^3. Pressures of B_2H_6 ranged from approximately 60 to 400 torr. Laser power was varied from 10 to 20 W, while irradiation times of 2–30 min were employed. In all cases immediate formation of a yellow boron hydride polymer was noted. The polymer generally formed on the window through which the laser beam entered, as well as on the cell walls near this window. Needlelike $B_{10}H_{14}$ crystals began to form on the cell walls shortly after irradiation commenced. Typical infrared spectra of a sample of diborane prior to irradiation, immediately following irradiation, and after removal of H_2 and residual B_2H_6 from the irradiated sample are shown in Figure 1. The vibrational bands present in the latter spectrum are attributable to either B_5H_9 or B_5H_{11}.[11] Furthermore, comparison of the intensity of the B_5H_9 spectral feature at 2610 cm^{-1} with that of B_5H_{11} at 2500 cm^{-1} indicated that in all cases B_5H_{11} accounted for less than 10% of total pentaboranes formed (with identical pressure/path length conditions, the 2610-cm^{-1} band of B_5H_9 and 2500-cm^{-1} band of B_5H_{11} are of comparable intensity). None of the irradiated samples of B_2H_6 revealed any evidence for the formation of B_4H_{10}.

A summary of the amounts of products formed under various experimental conditions is given in Table I. Several trends may be noticed upon examination of these data. For fixed diborane pressure and laser power, the amount of polymer formed increases as the irradiation time is lengthened. For instance, at ~200-torr B_2H_6 pressure and 10 W of CO_2-laser power incident on the cell, the polymer increases from 5.6% to 23% as the irradiation time is increased from 2 to 15 min. A similar trend is observed when the initial B_2H_6 pressure is ~60 torr. It may also be noted that the fraction of pentaborane decreases as the irradiation time increases (again note the 60- and 200-torr results). Furthermore, within the pressure range studied, most of the diborane which undergoes reaction is consumed in the initial few minutes of irradiation. For instance at 200-torr B_2H_6 pressure, 31% of the B_2H_6 reacts after 2 min, while only 54% has reacted after 15 min. Under conditions in which laser power and irradiation time are fixed (10-W power, 10-min irradiation time), but the diborane pressure is varied (93.5–385.1 torr); the decaborane yield is generally near 30%. This is substantially greater than the conversion observed in previous studies[9] and may be due to the higher laser fluxes used in the present case.

Table I. Conversion of B_2H_6 to Higher Boranes via CO_2-Laser Irradiation

initial B_2H_6 pressure, torr[a]	irradn time, min	laser power, W	fracn of B_2H_6 reacted	% conversion to B_5H_9, B_5H_{11}[b,c]	% conversion to $B_{10}H_{14}$[b]	% conversion to polymer[b]
59.8	2.0	20	0.435	48.5	20.7	30.8
59.9	10.0	20	0.503	28.3	29.8	41.9
60.1	30.0	10	0.446	59.6	8.3	32.1
93.3	2.0	20	0.518	38.2	19.5	42.3
93.6	10.0	15	0.539	40.9	26.7	32.4
93.5	10.0	10	0.326	32.0	35.3	32.7
145.8	10.0	10	0.501	56.0	33.1	10.9
197.1	2.0	10	0.306	60.2	34.2	5.6
199.9	10.0	10	0.438	55.8	27.2	17.0
199.7	15.0	10	0.536	48.1	28.9	23.0
250.1	10.0	10	0.562	47.1	36.1	16.8
385.1	10.0	10	0.415	56.1	32.0	11.9

[a] Pressure in 167.8-cm^3 irradiation cell. [b] The conversion is found from (B in higher boranes)/(B in B_2H_6 reacted). [c] B_5H_{11} accounts for less than 10% of the total pentaboranes formed.

Table II. Quantum Yields for $B_{10}H_{14}$ Produced by CO_2-Laser Irradiation of B_2H_6

initial B_2H_6 pressure, torr	irradn time, min	laser power, W	quantum yield[a]
59.8	2.0	20	1.1×10^{-4}
59.9	10.0	20	3.6×10^{-5}
60.1	30.0	10	5.5×10^{-6}
93.3	2.0	20	1.2×10^{-4}
93.6	10.0	15	6.0×10^{-5}
93.5	10.0	10	4.9×10^{-5}
145.8	10.0	10	1.2×10^{-4}
197.1	2.0	10	4.0×10^{-4}
199.9	10.0	10	9.8×10^{-5}
199.7	15.0	10	9.8×10^{-5}
250.1	10.0	10	1.5×10^{-4}
385.1	10.0	10	2.3×10^{-4}

[a] ($B_{10}H_{14}$ molecules formed)/(total number of photons absorbed by B_2H_6).

Table II summarizes the quantum yields for $B_{10}H_{14}$ formation obtained in the foregoing experiments. As may be noted, the quantum yields vary over almost two orders of magnitude. For fixed diborane pressure and laser power, the quantum yield decreases as the irradiation time is increased (note the 60- and 200-torr results). Furthermore, with irradiation time and laser power held constant (10 min, 10 W), the quantum yield increases as the pressure is increased. The best photon utilization for the production of $B_{10}H_{14}$ from neat B_2H_6 was 2500 photons/molecule. This value is almost an order of magnitude better than reported earlier.[9]

Since the copyrolysis of B_2H_6 and B_5H_9 yields $B_{10}H_{14}$ as the principal product,[3] laser-driven reaction of B_2H_6/B_5H_9 mixtures was viewed as a potentially better route to $B_{10}H_{14}$ than that via neat B_2H_6. B_5H_9 exhibits no infrared absorption at the R(16) line of the CO_2-laser 10.6-μm transition. Hence,

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Table III. Production of $B_{10}H_{14}$ via CO_2-Laser Irradiation of B_2H_6/B_5H_9 Mixtures

initial pressure, torr[a]		irradn time, min	laser power, W	fracn of B_2H_6 reacted	residual B_5H_9 pressure, torr[a]	% conversion to $B_{10}H_{14}$[b]
B_2H_6	B_5H_9					
93.6	15.0	10.0	10	0.259	13.5	46.3
197.0	60.0	2.0	10	0.129	59.3	66.1
199.9	59.9	10.0	10	0.324	60.0	66.9
199.9	29.9	10.0	10	0.396	37.5	49.3
284.9	88.6	10.0	10	0.384	83.1	58.4
285.4	49.2	10.0	10	0.423	57.0	62.5
285.3	88.6	3.0	8	0.091	87.7	58.8
285.2	88.7	3.0	10	0.228	86.6	61.0
354.2	106.3	3.0	10	0.205	101.6	45.3
360.0	107.9	3.0	8	0.064	106.7	67.5
360.0	107.9	10.0	10	0.376	98.8	45.0
360.0	64.9	3.0	10	0.267	66.4	47.3

[a] Pressure in 180.7-cm^3 reaction cell. [b] The conversion is found from (B in $B_{10}H_{14}$ formed)/(total B reacted).

Table IV. Quantum Yields for $B_{10}H_{14}$ Produced via CO_2-Laser Irradiation of B_2H_6/B_5H_9 Mixtures

initial pressure, torr		irradn time, min	laser power, W	quantum yield[a]
B_2H_6	B_5H_9			
93.6	15.0	10.0	10	9.0×10^{-5}
197.0	60.0	2.0	10	3.9×10^{-4}
199.9	59.9	10.0	10	2.2×10^{-4}
199.9	29.9	10.0	10	1.7×10^{-4}
284.9	88.6	10.0	10	3.4×10^{-4}
285.4	49.2	10.0	10	3.0×10^{-4}
285.3	88.6	3.0	8	7.3×10^{-4}
285.2	88.7	3.0	10	6.0×10^{-4}
354.2	106.3	3.0	10	5.5×10^{-4}
360.0	107.9	3.0	8	3.0×10^{-4}
360.0	107.9	10.0	10	2.9×10^{-4}
360.0	64.9	3.0	10	7.5×10^{-4}

[a] ($B_{10}H_{14}$ molecules formed)/(total number of photons absorbed by B_2H_6/B_5H_9 mixture).

absorption of laser radiation by B_2H_6/B_5H_9 mixtures is due solely to the B_2H_6. The results of irradiating a number of mixtures in which the total pressure and B_2H_6/B_5H_9 ratio were varied are summarized in Table III. It may be immediately noted that in all cases studied the yield of $B_{10}H_{14}$ exceeds the best conversion obtained with neat diborane. In fact, yields in excess of 65% are observed. Another interesting observation is that there is very little change between the initial and final pentaborane concentration, although a small amount of B_5H_{11} is detected following irradiation. In addition to an enhancement in the $B_{10}H_{14}$ yield, a substantial improvement in the quantum yield of $B_{10}H_{14}$ production is realized. The quantum yields are listed in Table IV. The number of photons required for production of each $B_{10}H_{14}$ molecule is as low as 1400.

An additional experiment was performed in which pure B_5H_9 vapor was irradiated with the CO_2 laser to determine whether reaction could be stimulated. The laser was tuned to the P(36), 10.6-μm transition (929.02 cm^{-1}), a frequency which coincides with a vibrational feature in B_5H_9.[11] Irradiation of a 100-torr sample of B_5H_9 with a power of 10 W for 20 min produced no change either in the infrared spectrum of the B_5H_9 or in the pressure in the cell. It appears no reaction occurs upon laser irradiation of B_5H_9 using the above conditions. This observation is consistent with the relatively high thermal stability of B_5H_9 and indicates that in copyrolysis of B_2H_6 and B_5H_9 initial reaction indeed occurs via fragments produced from B_2H_6.

As mentioned earlier, one of the isolable products associated with pyrolysis of B_2H_6 is B_4H_{10}.[3] In none of the laser-induced reactions was this product observed (a relatively strong infrared band at 2130 cm^{-1} would have revealed the presence of B_4H_{10}[11]). These observations may be reconciled in the following manner. B_5H_9 is known to be the predominant product in the high-temperature (250–300 °C) pyrolysis of B_2H_6,[12] whereas B_5H_{11} predominates at lower temperatures (180 °C).[13] Furthermore, at high temperatures dissociation of both B_4H_{10} and B_5H_{11} is favored.[3] In the mechanistic interpretation of the formation of higher boranes,[3] B_4H_{10} and B_5H_{11} dissociate via pathways 1 and 2. The unstable B_3H_7 and B_4H_8 intermediates presumably undergo subsequent reaction to form B_5H_9 by eq 3. Since little B_5H_{11} and no B_4H_{10} are detected

$$B_4H_{10} \rightleftarrows BH_3 + B_3H_7 \tag{1}$$

$$B_5H_{11} \rightleftarrows BH_3 + B_4H_8 \tag{2}$$

$$B_3H_7 + B_4H_8 \rightarrow B_2H_6 + B_5H_9 \tag{3}$$

in the laser-driven reaction of B_2H_6, it appears that sufficiently high temperatures are reached to cause dissociation of these species and prevent their accumulation. B_5H_9, on the other hand, is more thermally stable than either B_4H_{10} or B_5H_{11}, explaining its predominance.

4. Conclusions

The CO_2-laser-stimulated reaction of B_2H_6 and B_2H_6/B_5H_9 mixtures to prepare $B_{10}H_{14}$ appears to be a thermal process, an observation consistent with previous results.[8,9] However, in the present investigation better conversions to decaborane and improved photon utilization have been obtained for irradiation of neat B_2H_6. Furthermore, laser irradiation of B_2H_6/B_5H_9 mixtures has been reported for the first time. These studies have resulted in an even greater improvement in the production of $B_{10}H_{14}$. Conversions to $B_{10}H_{14}$ of greater than 65% of the material which undergoes reaction and photon requirements of less than 1400 per $B_{10}H_{14}$ molecule have been observed.

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Registry No. B_2H_6, 19287-45-7; B_5H_9, 19624-22-7; B_5H_{11}, 18433-84-6; $B_{10}H_{14}$, 17702-41-9.

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