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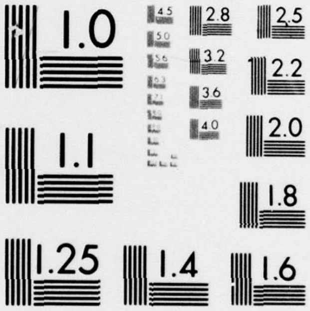

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FINAL REPORT

LASER INDUCED CHEMISTRY FOR PRODUCTION OF DECABORANE, $B_{10}H_{14}$, FROM DIBORANE, B_2H_6

By

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The goal of this research was to provide information concerning the feasibility of converting B_2H_6 to $B_{10}H_{14}$ with CW-CO_2 laser irradiation.

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INTRODUCTION

A. Background

Decaborane (14), $B_{10}H_{14}$, is an important starting material for the synthesis of carboranes, many of which have properties suitable for solid propellants and ballistic burn moderators. Decaborane is presently produced by pyrolysis of diborane, B_2H_6, at atmospheric pressure in either a static or a flow system arrangement.

Recently, Kompa, et. al., reported the CW-CO_2 laser induced conversion of B_2H_6 to higher molecular weight compounds such as icosaborane (16), $B_{20}H_{16}$, pentaborane -9, B_5H_9,and decaborane, $B_{10}H_{14}$.[1] Their work involved laser irradiation of B_2H_6 at initial pressures between 50 and 400 Torr. B_2H_6. The laser was made resonant to the ν_{14} wagging normal mode of $^{11}B_2H_6$ by tuning to the (R(16), 00°1 - 10°0) transition at 973 cm^{-1}. They reported high yields of icosaborane with low laser power ($\leq$ 8W) although no numerical results were provided. More importantly, they reported that in three out of their fourteen irradiations a different reaction occurred, one which appeared to be slower, resulting in predominately B_5H_9 and some $B_{10}H_{14}$. Again no numerical results were provided.

B. Objectives and Goal of this Research

The goal of this research was to provide information concerning the feasibility of converting B_2H_6 to $B_{10}H_{14}$ with CW-CO_2 laser irradiation. Several objectives were necessary to attain this goal. Firstly, the work of Kompa, et. al.,[1] needed to be repeated. This would include exploratory runs on B_2H_6 with the laser, laser cell development, development of analysis techniques and product characterization. The second objective would be to parameterize the reaction variables. This would include determination of product photon requirements as a function of the initial B_2H_6 pressure at constant power and intensity, determination of the initial photon requirements for various products and B_2H_6 conversion at constant pressure and the effect

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[1] H. R. Bachmann, H. Nöth, R. Rinck and K. L. Kompa, *Chem. Phys. Let.*, 29, 627 (1974).

of intensity. Subsequent to this phase of study a flow experiment was planned if the process looked economically promising for the laser induced preparation of $B_{10}H_{14}$. Thirdly, an experiment(s) would be designed to determine if the LIC (Laser Induced Chemistry) reactions were initiated by primary molecules of B_2H_6 having vibrational excitation due to multiphoton absorption or were just thermally generated subsequent to a V-T transfer. Fourthly, if it were found that conversion of B_2H_6 to $B_{10}H_{14}$ was not economically feasible with B_2H_6 absorption of CW-CO_2 irradiation then laser sensitization experiments would be attempted to attain that goal. Lastly, experiments which would give possible insight into the reaction mechanisms would be attempted. These could provide information on how to alter the LIC process to make the $B_2H_6 \rightarrow B_{10}H_{14}$ conversion more economical.

II. THE RESEARCH

A. Preliminaries and Parameterization of LIC Variables

The methods and procedures for completing several of the objectives are discussed in our first LIC paper which has been accepted for publication in Inorganic Chemistry. In this paper we describe the cells, analysis techniques, method of characterizing products and parameterization of a number of variables associated with the LIC of B_2H_6. We found significant differences from Kompa, et. al.'s[1] initial results. Some of these differences are explainable.

Kompa, et. al., reported the production of incoraborane, $B_{20}H_{16}$, when B_2H_6 was irradiated with the (R(16), 00°1-10°0) 973 cm^{-1} CW CO_2 laser line. In our work we never found $B_{20}H_{16}$, nor did we see luminescence. However, we did produce a solid material which has similar characteristics to $B_{20}H_{16}$ (except for color and melting point)[2] which we characterized as the known polymeric material (BH)[3]. High intensity CO_2 pulsed laser irradiation also gives this polymeric material accompanied by emission of the yellow luminescence[4] reported by Kompa and workers. Although we never produced $(BH)_n$ as the preferred product or saw the luminescence this could be attributed to lower intensities (beam temperatures). Since $(BH)_n$ has no known value the fact that all runs resulted in $B_{10}H_{14}$ and pentaborane and less $(BH)_n$ was initially promising.

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Laser-Induced Chemistry of Diborane

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Diborane was irradiated with the 973-cm^{-1} line of a CW CO_2 laser. The products $B_{10}H_{14}$, B_5H_9, B_5H_{11}, $(BH)_n$, and H_2 resulted in all runs. The number of photons required to produce or transform one molecule of $B_{10}H_{14}$, $B_5H_9 + B_5H_{11}$, H_2, and B_2H_6 was determined at pressures between 64 and 510 Torr with the laser power maintained at 7.85 W. The yields of $B_{10}H_{15}$, $B_5H_9 + B_5H_{11}$, and H_2 produced or B_2H_6 transformed were measured as a function of illumination time at a laser power of 8 W and an initial B_2H_6 pressure of 410 Torr. The number of photons required to produce one molecule of $B_{10}H_{14}$, $B_5H_9 + B_5H_{11}$, and H_2 or transform one molecule of B_2H_6 was determined to be 22000, 287, 156, and 156 at time zero, respectively. No evidence for a chain process was found, the reaction was not accompanied by light emission, and $B_{20}H_{16}$ was not produced.

Introduction

Although available for some time, the advantages of the high intensity and monochromacity of the [redacted] laser are just beginning to be realized in synthetic chemistry.[3-5] The ability to enhance desired reaction channels is one of the goals of any synthetic chemist. The multitude of reaction channels opened by thermoequilibrium processes often results in not only many undesirable products but products that may be difficult to separate from those desired. The laser has great potential for simplifying as well as enhancing the yield of desired product during chemical transformation. This intense monochromatic source enables multiple photon absorption which can enhance rate constants orders of magnitude by effectively decreasing the activation energy.

Kompa et al. presented interesting data in 1974 in which CW CO_2 laser experiments on diborane were outlined.[6] Using the R-16 (973 cm^{-1}) line for excitation, they excited the ν-14 wagging mode of B_2H_6.[7] They reported that upon lasing B_2H_6 at various initial B_2H_6 pressures and laser power 11 out of 14 experiments resulted predominantly in the production of icosaborane ($B_{20}H_{16}$). They reported that when $B_{20}H_{16}$ was produced luminescence was also observed and the reaction appeared to be a high quantum yield chain process. However, in 3 out of 14 experiments they reported a slower process not

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resulting in icosaborane production, but pentaborane(9) (B_5H_9) and decaborane ($B_{10}H_{14}$). No explanation was offered for the occurrence of two different sets of reactions under the same experimental conditions. Decaborane is a starting material for the synthesis of carboranes, which have application as burn moderators for solid propellants. Since Kompa et al.[6] experiments reported some $B_{10}H_{14}$ product, we thought it worthwhile to repeat the work to determine if we could enhance the occurrence of the slower reaction resulting in $B_{10}H_{14}$ formation in preference to $B_{20}H_{16}$. Our results disagree with those Kompa et al. reported.

Experimental Section

The diborane, obtained from Callery Chemical Co., was stated to be at least 99 mol % pure at the time of shipment. Shipment at ambient temperatures and storage in a freezer between runs results in some decomposition. A minimum of four trap-to-trap distillations were made utilizing a glass vacuum manifold before a sample was considered acceptable. Diborane was first separated from noncondensable H_2 by application of a liquid nitrogen (77 K) trap and subsequent pumping. This was followed by several dry ice–acetone (195 K) to liquid nitrogen transfers to remove higher molecular weight boranes. Infrared[8,9] and mass spectra[10] of the purified diborane did not indicate the presence of any impurities. When the purified diborane was not in use it was retained in a vacuum bulb in a 193 K freezer. The foregoing purification process was always repeated even on the previously purified 193 K stored diborane before each days' run.

The laser cell design required vacuum operation and quick disassembly for cleaning. The laser cells were constructed from $1^7/_8$ in. o.d. and $1^1/_2$ in. i.d. Pyrex glass pipe. They were fitted with a vacuum stopcock and a detachable side-arm vial for condensations. Ends of the cells were fitted with 6.5 mm thick NaCl windows. Each window was vacuum sealed to ground glass ends of the cells by two Viton O-rings fitted into a stainless steel O-ring retainer grooved on both sides. The windows were held in place by aluminum end caps secured end to end by four rods and bolts. Each assembly has a path length of approximately 10 cm and a volume of 126–132 cm^3. Only Kel-F halocarbon grease was utilized. The cells were vacuum leak checked prior to use, always purged with 75–100 Torr of purified B_2H_6 for several minutes, reevacuated, and then charged with the desired B_2H_6 pressure. Pressure was determined with a simple Hg manometer.

The same charging vacuum manifold was utilized subsequent to the runs to determine the pressure of H_2, pentaborane, and B_2H_6 by a simple differential pressure technique which only required applying liquid nitrogen, dry ice–acetone, and room temperature baths to the detachable side-arm vial and reading respective cell pressures. Evacuation of the cell enable condensation of the $B_{10}H_{14}$ into the detachable side arm at salt–ice bath temperatures which could be weighed. $B_{10}H_{14}$ purity was determined by infrared spectroscopy[8] and melting point,[11] (BH)*n* was characterized by noting its infrared spectrum, lack of a melting point, deliquescence properties, and reaction with H_2O to form an acid solution.[12] The B_5H_9 and B_5H_{11} mixture was characterized by infrared spectroscopy and mass spectrometry.[13]

The laser was a Coherent Radiation Model 42 CW CO_2 laser fitted with a Model 435 grating. Single-line operation was monitored with an Optical Engineering CO_2 spectrum analyzer. Power was monitored with Coherent Radiation power meters whose output was displayed on a strip chart recorder. Power was maintained at a constant level during runs by placing a beam splitter prior to the reaction cell which enabled monitoring of approximately 3% of the power irradiating the cell. Power loss by reflection and absorption through each NaCl window was 0.5–0.65 watts. Beam diameter was nominally 0.9 cm.

Results and Discussion

We have exposed B_2H_6 to the 973-cm^{-1} R-16 line of a CW CO_2 laser more than 40 times. Not once was luminescence observed or evidence of a chain process noted as found by Kompa et al.[6] Icosaborane, $B_{20}H_{16}$, was never found as a product. We found the slower reaction produced a B_5H_9 + B_5H_{11} mixture and $B_{10}H_{14}$ in all experiments. A material which we identify as the infamous yellow solids polymer $(BH)_n$ was also produced in all runs.[12]

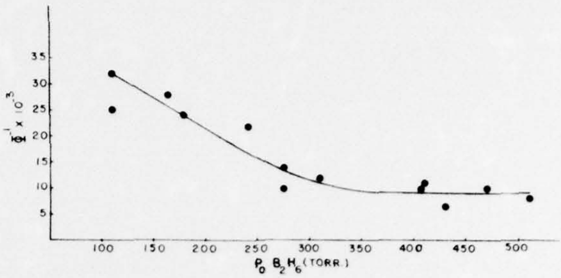

Figure 1. Number of photons required to produce one molecule of $B_{10}H_{14}$, Φ^{-1}, as a function of initial B_2H_6 pressure. Laser power 7.85 W.

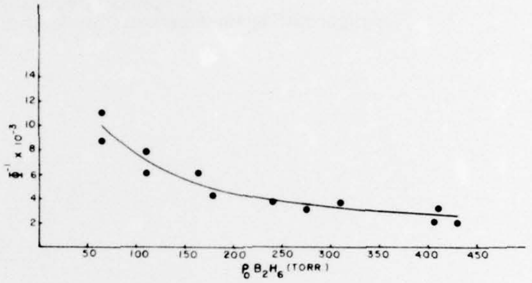

Figure 2. Number of photons required to produce one molecular unit of B_5H_9 + B_5H_{11} mixture, Φ^{-1}, as a function of initial B_2H_6 pressure. Laser power 7.85 W.

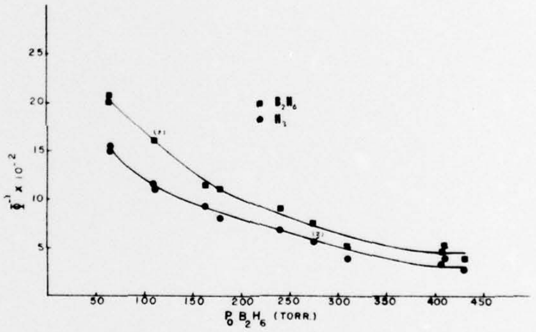

Figure 3. Number of photons required to produce one molecule of H_2 (circles) or to convert one molecule of B_2H_6 (squares), Φ^{-1}, as a function of initial B_2H_6 pressure. Laser power 7.85 W.

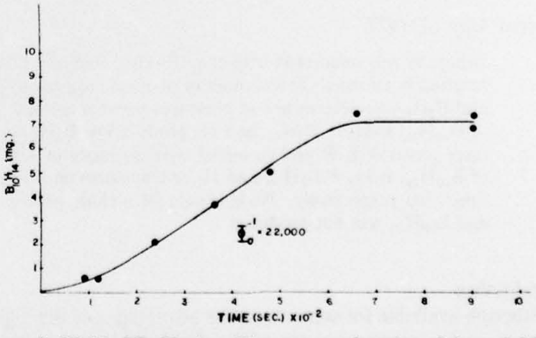

Figure 4. Yield of $B_{10}H_{14}$ in milligrams as a function of time. Initial B_2H_6 410 Torr. Laser power 8 W. Initial slope gave a value of 22 000 photons required for each $B_{10}H_{14}$ molecule produced, Φ_0^{-1}.

Temperature increases of as much as 10 °C were noted at times in the higher pressure runs with the glass cells. Several runs made initially in heavy stainless cells (large heat sink) showed no signs of temperature increase and the same products were produced.

Figures 1, 2, and 3 depict the variation in the number of photons required to produce a product molecule of $B_{10}H_{14}$, B_5H_9 + B_5H_{11}, and H_2 or to transform a molecule of B_2H_6,

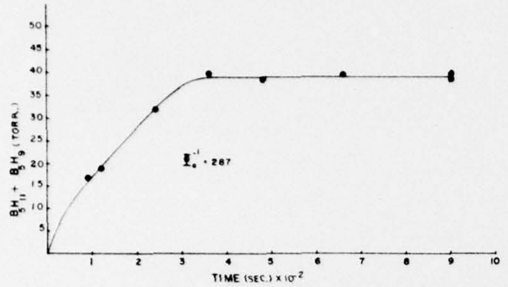

Figure 5. Yield of pentaborane mixture in Torr as a function of time. Initial B_2H_6 pressure 410 Torr. Laser power 8 W. Initial slope gave a value of 287 photons required for each pentaborane molecular unit produced, Φ_0^{-1}.

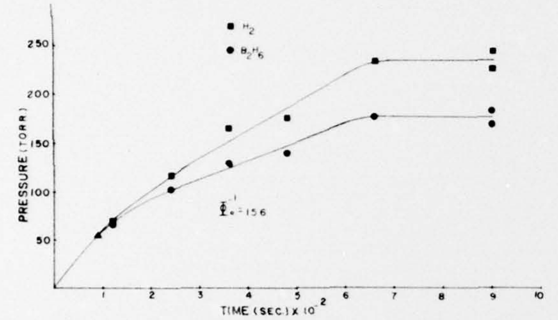

Figure 6. Yield of H_2 (squares) and of B_2H_6 (circles) converted in Torr as a function of time. Initial B_2H_6 pressure 410 Torr. Laser power 8 W. Initial slope gave a value of 156 photons required per H_2 molecule produced or B_2H_6 molecule converted, Φ_0^{-1}. Triangle indicates same value.

respectively, as a function of initial B_2H_6 pressure. Laser input power after the first window was nominally 7.85 W and intensity was 12.3 W cm^{-2}. All show a pronounced requirement for an increased number of photons as the B_2H_6 pressure decreases. Photon requirements appear to be too high to support a chain mechanism interpretation. Figures 4, 5, and 6 show yields for formation of $B_{10}H_{14}$, $B_5H_9 + B_5H_{11}$, and H_2 and transformation of B_2H_6, respectively, as a function of time. Initial B_2H_6 was 410 Torr. $B_{10}H_{14}$ chemical yields varied from 5 to 13%, with the higher yields coming at higher initial B_2H_6 pressures. Laser power and intensity were maintained at 8 W and 12.6 W cm^{-2}, respectively. In Figure 4 the yield was extrapolated through the origin because $B_{10}H_{14}$ crystals were visible as early as 30 s into the runs although not measurable by our technique. The initial slopes are related to the initial photon requirements, Φ_0^{-1}, indicated on the figures. The magnitude of the initial photon requirements also do not support a chain-type mechanism. The fact that $B_{10}H_{14}$ initial photon requirements are higher than those averaged over time seems to imply a multistep mechanism and/or a thermal process. Pentaborane yields are nearly 50% of maximum after 2 min as compared to less than 10% for $B_{10}H_{14}$. Similar early H_2 formation and B_2H_6 conversion yields with identical Φ_0^{-1}'s also indicate the pentaboranes are produced at a faster rate initially than $B_{10}H_{14}$ and both or one may be required as a stable intermediate for $B_{10}H_{14}$ formation.

We have not concluded whether the process is thermal or not. Whereas B_4H_{10} and B_5H_{11} are both generally associated with thermal processes only the latter was detected.[14] Experiments are underway to determine if a thermal process is involved. No explanation can be offered at this time why these results differ from those reported previously by Kompa et al.[6] Increasing intensity to 169 W cm^2 or introducing approximately 2 Torr of O_2 (to emulate leaky cells) did not result in the chain process they reported.

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Registry No. B_2H_6, 19287-45-7; $B_{10}H_{14}$, 17702-41-9; B_5H_9, 19624-22-7; B_5H_{11}, 18433-84-6; H_2, 1333-74-0.

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Continuous Wave CO_2 Laser Induced Chemistry of Diborane. A Thermal Reaction

Sir:

The idea of using lasers in chemical synthesis to open reaction channels not accessible at thermal equilibrium is attractive. Bachmann, Nöth, Rinck, and Kompa[1] generated con-

Table I. Chopped and Unchopped CW-CO_2 Laser Irradiation of B_2H_6 Comparison at 410-Torr B_2H_6 Initial Pressure

Run	Chopper frequency, Hz	Laser power, W	Window loss, W	Power to sample during open time, W	Intensity to sample during open time, W/cm² [a]	Total run time, s [b]	Pentaborane yield, Torr	$B_{10}H_{14}$ yield, mg [c]	B_2H_6 consumed, Torr
1	Open	8.6	0.6	8	12.6	660	40	7.5	178
2	Open	8.6	0.6	8	12.6	325	38	3.8	126
3	Open	8.6	0.6	8	12.6	313	38	3.9	126
4	25	8.6	0.6	8	12.6	685	11	None	22
5	38	8.6	0.6	8	12.6	660	9	None	16
6	1600	8.6	0.6	8	12.6	685	4	None	10
7	Open	4.3	0.4	3.9	6.0	660	7	None	20
8	45	12.6	0.9	11.7	18.4	685	22	0.4	64
9	41	13.0	1.0	12.0	18.9	660	24		59
10	Open	6.6	0.5	6.1	9.6	660	28	1.2	80

[a] Based upon 0.9-cm beam diameter. [b] When chopping, the effective irradiation time is run time multiplied by open fraction. [c] $(BH)_n$ yields were not determined. $(BH)_n$ was not visible when there was no $B_{10}H_{14}$.

siderable attention in 1974 when they reported the use of a tuned CW-CO_2 laser to synthesize larger molecules, including $B_{20}H_{16}$ (icosaborane), $B_{10}H_{14}$ (decaborane), and B_5H_9 (pentaborane-9) from diborane. They reported that $B_{20}H_{16}$, essentially the sole reported product in 11 out of 14 experiments, was produced in a chain process. Furthermore, $B_{10}H_{14}$ and B_5H_9 were said to have lower probability of production and occurred in the product mixture in only 3 out of 14 experiments. Since B_4H_{10} and B_5H_{11}, normally found among the products of B_2H_6 pyrolysis experiments,[2] were not detected and the reaction vessel temperature did not increase, it was concluded that the reactions were initiated by a controlled vibrational excitation.

Previous studies[3] in our laboratory have revealed no evidence for the production of $B_{20}H_{16}$ under similar conditions. A yellow white solid was produced that has characteristics similar to $B_{20}H_{16}$ (except for melting point and color).[4] The melting point of the hygroscopic solid was determined in a drybox in total. It did not melt below 250 °C, whereas $B_{20}H_{16}$ melts at 199 °C. The infrared analysis of the solid was performed upon deposits on the window after removing H_2, B_5H_9, B_5H_{11}, B_2H_6, and $B_{10}H_{14}$. It was not required to open the cell for the analysis. The spectrum was found to be identical with that reported by Rinck[5] and is characteristic of a B–H stretch. This substance was characterized as $(BH)_n$ polymer.[6] It was further determined that a large number of photons were required to produce the product molecules, especially $B_{10}H_{14}$ ($\sim 10^2$–10^4). These large photon requirements suggested a complex and/or thermal mechanism.

The present work was carried out to determine if vibrationally excited molecules produced by multiple photon absorption were involved directly or if a thermal process was taking place subsequent to vibration-translational energy transfer from the laser excited B_2H_6. To make this distinction the laser beam was chopped with a slotted wheel (2.54-cm slots, 2.85-cm teeth, 47.1% open) driven by a variable dc motor. The procedure for preparation and analysis of samples in the cells has been described previously.[3] The laser was tuned to the (R(16), 00°1–10°0) line at 973 cm^{-1}.

Table I compares the chopped and unchopped results at 410-Torr initial pressure. Comparing the first six listings one notes that chopping inhibits reaction substantially under our experimental conditions. However, the most important result is the fact that, when the same number of photons was passed through the system at the same power and intensity for unchopped (open) and chopped runs, the same result was not produced (runs 2 and 3 vs. runs 4 and 5). This is inconsistent with predominantly vibrationally controlled chemical processes. The results can be interpreted in terms of a thermally derived process in which the reaction rate is dependent upon the temperature within the beam envelope. Using the formulation of Steverding et al.[7] a photoabsorption cross section for B_2H_6 of 3×10^{-20} cm^2 derived from its infrared spectrum, and a calculated diffusion coefficient of 1×10^{-4} m^2/s, we estimate the temperature in the beam envelope to be 500 K. This estimated temperature is consistent with thermally derived processes involving diborane to produce the products found. Comparisons of chopped runs 4–6 with unchopped runs 7 and, chopped runs 8 and 9 with unchopped run 10 indicates that average intensity (or average temperature) appears to govern the product yield.

As additional evidence we have carried out sensitized experiments involving the laser irradiation of SF_6 and B_2H_6 mixtures. SF_6 (11 Torr) was added to B_2H_6 (400 Torr) and the laser output was made resonant with the ν_3 (933 cm^{-1}) fundamental of SF_6 by tuning to the (P(32), 00°1–10°0) line.[8] Power and intensity to the sample were maintained at 8 W and 12.6 W/cm^2, respectively. The same products were found as occurred when B_2H_6 was illuminated directly with the R-16 (973 cm^{-1}) line.[3] However, the production of $(BH)_n$ was visibly greater than in the neat B_2H_6 experiments. Upon opening the beam stop, $(BH)_n$ polymer could be initially generated in a (visibly) faster reaction than those leading to other products. This faster reaction ceased quickly although the beam was on. Interrupting the beam for a short time and opening the beam stop again could generate another flurry of polymer. No reaction was found when 400 Torr of neat B_2H_6 was irradiated under these conditions. It would seem to follow that these reactions must be thermal because a *V–T* transfer is required for the energy to reach the B_2H_6.

The faster reaction producing $(BH)_n$ under sensitized conditions is interesting especially at these high pressures. The same results were found at 25 Torr of B_2H_6 with 5 Torr of SF_6 using the P-20 (944.2 cm^{-1}) line with 6.1-W power and 15.9-W/cm^2 intensity. The absorption cross section of SF_6 is several orders of magnitude greater than B_2H_6 and results in total energy deposition within a few millimeters path length. Even though it would seem a *V–T* transfer is required to produce this faster reaction leading to $(BH)_n$, the nature of this process is open to question and requires future study. High intensity pulsed CO_2 laser irradiations of 50–400 Torr of neat B_2H_6 with the R-16 line have also been reported to result predominantly in formation of the yellow white polymeric solids in a faster reaction.[9]

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C. Brief Summaries of Other Work Done

1. CW-HF Laser Irradiation of B_2H_6

CW-HF laser irradiation of B_2H_6 with initial pressures between 200 and 500 Torr. were carried out. Powers of 7.2 W with the HF band center at approximately 3700 cm^{-1} produced no change in the B_2H_6. A combination of a broad many lined output, and a weak absorption at 3650 cm^{-1} did not result in high enough beam temperatures to bring about reaction.

2. CW-DF Laser Irradiation of B_2H_6

CW-DF laser irradiation of B_2H_6 with initial pressures between 100 and 410 Torr. were made. Powers of 3.9 W with the DF band center at approximately 2650 cm^{-1} produced results that were strongly intensity dependent. Intensities of 7 8 W/cm^2, corresponding to 3.9W incident power with a .125 cm beam radius resulted in predominately $(BH)_n$. Reduction of intensity to 7.8 W/cm^2 gave results similar to those of R-16 CW-CO_2 laser irradiation of B_2H_6 with the slower processes producing pentaborane and decaborane becoming more probable. The expense of DF laser operation does not appear to make this process economically feasible. However, variables are being parameterized.

3. CW-CO_2 Laser Irradiation of B_5H_9

This was carried out to determine if B_5H_9 could be converted and whether it would follow a reaction path to $B_{10}H_{14}$ or $(BH)_n$. Unfortunately only $(BH)_n$ was produced. Strong intensity and power dependences were noted. $(BH)_n$ production became rapid with the slighest increase of power and intensity above our usual 8 W and 12.6 W/cm^2. Mixtures of B_5H_9 and B_2H_6 along with B_5H_9 and SF_6 are planned for the future although the latter would not seem promising because it should result in increased $(BH)_n$ production as the beam temperature is increased by addition of the very strongly absorbing SF_6.

4. CW-CO_2 Laser Irradiation of $SF_6 + B_2H_6$ Mixtures

The laser was made resonant with the ν_3 fundamental of SF_6 by tuning to the (P(34), 00°1-10°0) 933 cm^{-1} line. The results were by far the most encouraging of all of our attempts to arrive at a synthesis of $B_{10}H_{14}$ from B_2H_6 by way of LIC. Yields of $B_{10}H_{14}$ were often increased by factors varying from 1-1/3 to 3 relative to those found with R-16 irradiation of B_2H_6 directly. However, even when the power, 8W, and intensity, 12 W/cm^2, were maintained, large variations in the amount of $(BH)_n$ and $B_{10}H_{14}$ were found from sample to sample. $(BH)_n$ production appeared to be decreased when the initial B_2H_6 pressure was maintained above 400 Torr. (SF_6 held at approximately 11 Torr.). At lower pressures $(BH)_n$ was produced initially in a great burst as the beam entered the sample, accompanied by the emission of yellow luminescence, followed by the slow methodical production of $B_{10}H_{14}$ (usually enhanced) and B_5H_9. Interestingly no B_5H_{11} was found as a product. There may be a correlation between $(BH)_n$ production and B_5H_{11}. Much work needs to be carried out on this sensitized reaction to find the best compromise for $B_{10}H_{14}$ synthesis. Simple intensity reduction may be very profitable.

5. Low Temperature CW-CO_2 Irradiation of B_2H_6

R-16 irradiation of B_2H_6 was carried out at -67± 4°C with a laser power of 8 W and intensity of 12.6 W/cm^2. The cell was similar in design to those described in Paper 1 except it had a double wall jacket with entrance and exit connections for liquid circulation. The cell was cooled by chilled methanol which had been passed over copper coils through which liquid nitrogen was circulated. No solids were produced at this low temperature. The only detected product was pure B_5H_{11} which was characterized by IR spectroscopy. More work definitely needs to be carried out to determine the significance of this result in terms of a reaction mechanism. Increasing temperatures in steps hopefully should reveal some of the complex mechanism associated with the LIC of B_2H_6.

III. DISCUSSION AND CONCLUSIONS

The preparation of $B_{10}H_{14}$ from B_2H_6 by direct laser irradiation of the ν_{14} B_2H_6 wagging made was not found to be economically feasible. The process required a large number of photons and was found to be occuring by a thermal type mechanism. Although the resonant laser energy was deposited into vibrational energy initially it was quickly degraded by V-T transfer. Application of the formulation of Steverding, et. al.,[7] resulted in a calculated beam temperature of 500°K and an average vibrational excitation ($\bar{n}$) of .06 - .07 above the ground n = 0 level.

The LIC of SF_6 + B_2H_6 mixtures looked more economically promising because of the increased yields of $B_{10}H_{14}$. However, since this is still a thermal process involving V-T transfer again we may be faced with a large photon requirement. Work needs to be done in parameterizing the variables associated with these reactions.

Although it appears that the laser is giving us thermo chemistry at these high pressures it should be noted that laser thermally generated processes do not involve surfaces and can result in somewhat different reaction channels being utilized. Work involving identification of intermediates such as with our low temperature laser irradiation experiments needs to be continued in order to give us a proper comparison with the classical thermo chemistry results.

Overall from this brief excussion into LIC it appears that synthesis requiring many steps will continue to be thermally derived, comparable to classical results unless some surface effect causes the classical to be different. However, high cross section processes involving one step mechanisms, that is reaction after a relatively small number of collisions with a vibrationally excited species, still offers promise.

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