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(32) In physical terms, metal particles in the size range 10–1000 Å (called microcrystals) usually display one broad absorption band, which arises from a collective excitation of all free electrons in the particle and can be described in terms of a free-electron gas model.[11] This is to be contrasted with the discrete absorptions of "molecular aggregates" containing a small number of atoms, the mute point being: how many metal atoms constitute "small", within the framework of these discussions? Briefly, collectively displayed free electrons see no repulsive force in the bulk metal and hence zero resonant frequency. However, surface polarization effects in microcrystals produce a field opposite to the electric field of the incident light and cause an absorption maximum (called a plasmon absorption) at finite frequencies.[11] For spherical particles which are small compared to the wavelength of the incident light and which are embedded in a nonabsorbing medium with dielectric constant ϵ_m, the plasmon frequency ω_p is defined by $\epsilon_1(\omega_p) = -2\epsilon_m$ where ϵ_1 is the real part of the dielectric function of the particle.[11] For finite particle density the interaction between the microcrystals must be taken into account by using $\epsilon_1(\omega_p) = -\epsilon_m(2 + Q)/(1 - Q)$ where Q is the volume fraction of small, spherical particles.[11] This effect causes a *long wavelength shift* of the absorption maximum as the size and packing of the particles increases.
(33) We note with great interest that in the emission band system of Ag_2 produced in a silver discharge, Shin-Piaw et al.[26b] found evidence for about 30 bands in the 410–470-nm visible system, degrading to the red, most of which grouped into well-marked sequences which could be well-represented by the usual expression involving the vibration quanta and frequencies of the lower and upper states of the so designated (A–X) system. However, Shin-Piaw et al.[26b] discovered 11 *weak and complicated* bands in a region succeeding the aforementioned band systems at 480.7, 481.1, 486.1, 488.4, 491.5, 491.7, 495.8, 492.2, 499.4, 501.6, and 502.4 nm as well as some complications in the long-wavelength side of the 410–470-nm region which could not be fit into the (A–X) vibrational progression for Ag_2. It was suggested at the time that these bands may be due to polyatomic molecules of silver.[26b] On the basis of our experiments with argon-entrapped Ag_n (where $n = 2–7$) we suggest that the silver discharges of Shin-Piaw et al.[26b] could in fact contain some higher Ag_n clusters. On these grounds further studies of the emission and absorption spectra of gaseous silver clusters Ag_n with $n > 2$ seem justified.
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(40) Recent, quantitative "silver concentration" experiments in krypton matrices have confirmed our stoichiometric assignments for $Ag_{2,3,4}$ based on quantitative "photoaggregation kinetic experiments".[36]
(41) We are presently attempting to simulate these observations by SCF–Xα–SW transition-state molecular orbital calculations for $Ag_{2,3,4,5,6}$.[38]
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(44) We note here that Gruen and Bates[18g] recently reported optical spectra for sputtered silver atoms in Ne and Ar matrices at 5 and 13 K, respectively. By comparison with our photoaggregation/silver concentration/bulk annealing studies, observed bands at 280.5/270.5 and 440.0/244.0/237.5 nm assigned to Ag_2 in Gruen and Bates' optical spectra (Ar matrices) are reassigned to Ag_4 and Ag_3 clusters, respectively.

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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}, $(BH)_m$, 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 22 000, 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 chemical 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]

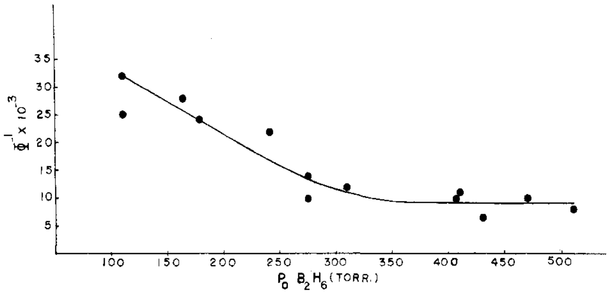

Figure 1. Number of photons required to produce one molecule of $B_{10}H_{14}$, Φ^{-1}, as a function of initial B_2H_6 pressure. Laser power 7.85 W.

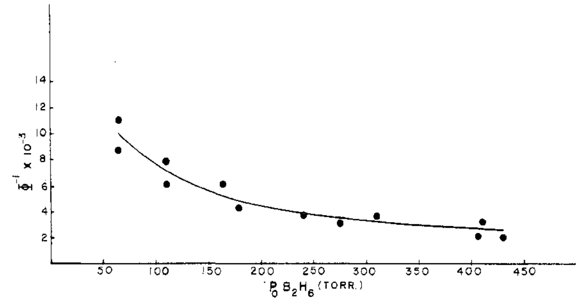

Figure 2. Number of photons required to produce one molecular unit of B_5H_9 + B_5H_{11} mixture, Φ^{-1}, as a function of initial B_2H_6 pressure. Laser power 7.85 W.

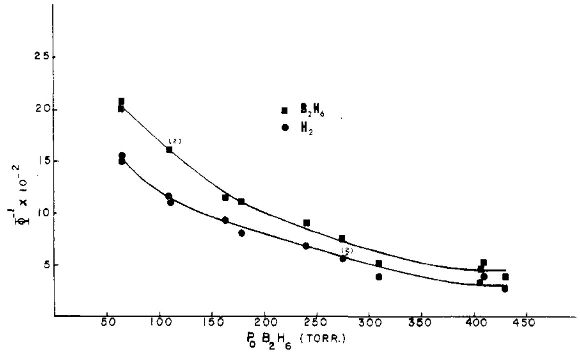

Figure 3. Number of photons required to produce one molecule of H_2 (circles) or to convert one molecule of B_2H_6 (squares), Φ^{-1}, as a function of initial B_2H_6 pressure. Laser power 7.85 W.

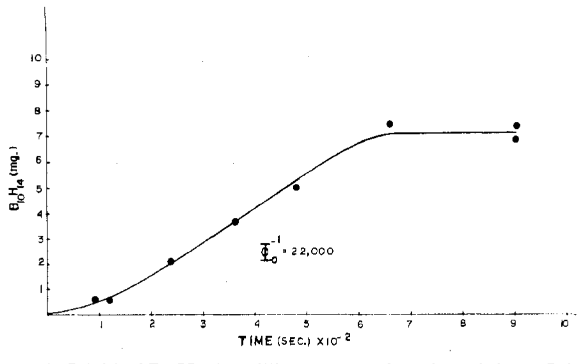

Figure 4. Yield of $B_{10}H_{14}$ in milligrams as a function of time. Initial B_2H_6 410 Torr. Laser power 8 W. Initial slope gave a value of 22 000 photons required for each $B_{10}H_{14}$ molecule produced, Φ_0^{-1}.

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,

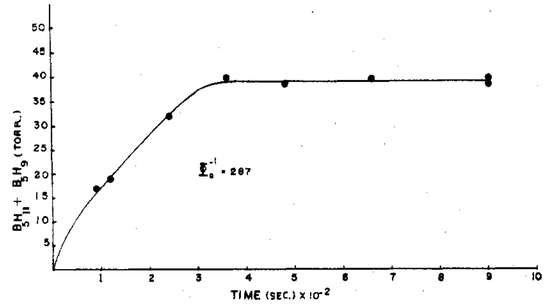

Figure 5. Yield of pentaborane mixture in Torr as a function of time. Initial B_2H_6 pressure 410 Torr. Laser power 8 W. Initial slope gave a value of 287 photons required for each pentaborane molecular unit produced, Φ_0^{-1}.

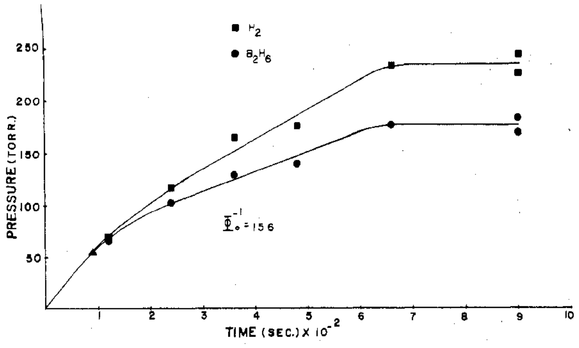

Figure 6. Yield of H_2 (squares) and of B_2H_6 (circles) converted in Torr as a function of time. Initial B_2H_6 pressure 410 Torr. Laser power 8 W. Initial slope gave a value of 156 photons required per H_2 molecule produced or B_2H_6 molecule converted, Φ_0^{-1}. Triangle indicates same value.

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.

References and Notes

(1) This research constitutes partial fulfillment of the B.S. degree requirements of S.S. who has been designated as a 1977 predoctoral NSF Fellow.
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