# Laser Initiated Thermal Synthesis of Triethylborane

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Olefin hydroboration with diborane has been extensively studied in the liquid phase in the presence of a catalytic ether solvent or similar weak base [1, 2]. In transmetallation experiments, $B(C_2H_5)_3$ has been prepared by treating $KBF_4$ or $BF_3$ with $Al(C_2H_5)_3$ [3, 4]. Little work has been done involving the gas phase. Previous experiments in the gas phase have not proved successful for the preparation of trialkylboron compounds [5, 6] in general, requiring elevated temperatures, long time intervals and producing low yields of the trialkylborane. Under carefully controlled conditions, simple alkenes in the presence of diborane in excess react in the gas phase to give mono and dialkylboranes in yields of around 60% and 35%, respectively [7]. Other experiments in the gas phase have used Group VIII metals as catalysts to obtain $B(C_2H_5)_3$ [8].

The photoinitiation of thermal explosions using infrared lasers to affect chemical reactions in the gas phase has been used successfully in several reactions. For example, $SF_6$ in mixtures with polyatomic molecules [9], the isomerization of methyl isocyanide [10], the combustion of $CH_4$–$O_2$ mixtures using $SF_6$ as a resonant absorber [11], the irradiation of ethyl iodide [12] and the single pulse irradiation of $NH_3$–$O_2$ mixtures [13]. The processes occur due to the high temperatures that can be obtained in a very short time which are sufficient to trigger a thermal explosion.

Because of the low yields and long time intervals required by the standard thermal synthesis of $B(C_2H_5)_3$ from gaseous $B_2H_6$ and $C_2H_4$, the idea of the present study was to develop a convenient method of synthesis in the gas phase using an infrared source to initiate the reaction. In this paper the laser induced synthesis of $B(C_2H_5)_3$ is reported. Gas phase mixtures of $B_2H_6$ and $C_2H_4$ of different compositions are irradiated with a cw $CO_2$ laser. By tuning the laser frequency to coincide simultaneously with the bands of fundamental frequencies $\nu_{14}$ of $B_2H_6$ and $\nu_7$ of $C_2H_4$, a thermal explosion is initiated. The reaction results in the complete disappearance of the $B_2H_6$ from the mixture and the formation of $B(C_2H_5)_3$ in yields of up to 91%. The whole process occurs within the first second of irradiation.

## Experimental

Diborane was synthesized using methods described in the literature [14] and purified by trap-to-trap distillation (–80 °C to –190 °C) in a vacuum system. $B_2H_6$ was separated first from noncondensible $H_2$ using a liquid nitrogen trap at –190 °C and subsequent pumping. This was followed by several dry ice-acetone (–80 °C) to liquid nitrogen transfers to remove higher boron hydrides. Infrared spectra of the purified diborane did not indicate the presence of impurities. $C_2H_4$ (99.98% purity from Matheson) was used without further purification.

The cell used was designed for vacuum operation and quick disassembly and cleaning. It was made of pyrex with a volume of 225 $cm^3$ equipped with a cold finger. KBr windows were attached to the cell with epoxy adhesive. The cell was vacuum leak checked prior to use, purged with a 50–100 Torr of $B_2H_6$, reevacuated and charged with the desired $B_2H_6$–$C_2H_4$ mixture sample. Pressures were measured with a Hg manometer. The cell fitted directly into the sample compartment of a Perkin-Elmer infrared spectrophotometer model 735B. Infrared spectra could be conveniently recorded prior to and following irradiation, as well as during various phases of the separation of the volatile components generated. The analysis of the reaction mixture after the irradiation indicated the formation of $H_2$, total disappearance of $B_2H_6$, remains of $C_2H_4$ in excess, small amounts of a solid polymeric material and liquid $B(C_2H_5)_3$. A vacuum system with sections of calibrated volume was utilized subsequent to the irradiations to determine the amounts of the individual components.

Separation of the 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 a 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 up to room 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 toluene-liquid nitrogen (–95 °C)

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TABLE I. Irradiation of $B_2H_6$–$C_2H_4$ Mixtures with a cw $CO_2$ Laser.

| Before Irradiation | | | | After Irradiation | | Weight | % Yield |
|---|---|---|---|---|---|---|---|
| P($B_2H_6$) (Torr) | P($C_2H_4$) (Torr) | Composition | P(total) (Torr) | P($H_2$) (Torr) | P($C_2H_4$) (Torr) | $B(C_2H_5)_3$ (mg) | $B(C_2H_5)_3$ |
| 24.5 | 295.5 | 1:12 | 320 | 18 | 169 | 67.7 | 91 |
| 32 | 288 | 1:9 | 320 | 39 | 140 | 55.8 | 56 |
| 46 | 274 | 1:6 | 320 | 86 | 127 | 48.2 | 34 |
| 80 | 240 | 1:3 | 320 | 172 | 105 | 36.0 | 14.5 |
| 69 | 386 | 1:6 | 455 | 130 | 188 | 63.9 | 30 |
| 23 | 137 | 1:6 | 160 | 37 | 65 | 25.0 | 34.5 |

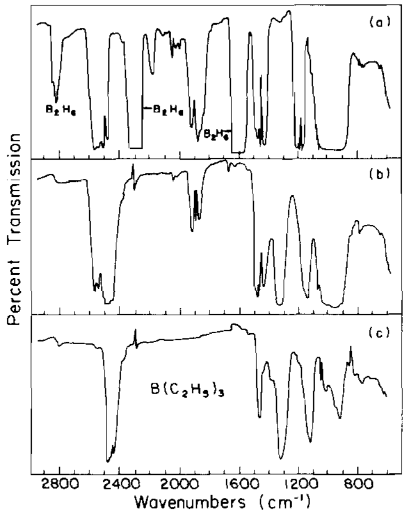

Fig. 1. Infrared transmission spectra of the $B_2H_6$–$C_2H_4$ mixture (1:6) (a) before irradiation, (b) immediately following irradiation with the P(20) line of the 10.6 μm $CO_2$ laser transition (944.21 $cm^{-1}$), and (c) after removal of the unreacted $C_2H_4$ and the $H_2$ generated from the irradiated sample.

slush allowed the pressure of residual $C_2H_4$ to be determined. At this point only $B(C_2H_5)_3$ and boron hydride polymer remained in the cold finger. The $B(C_2H_5)_3$ was distilled *in vacuo* into a preweighed sample tube immersed in liquid $N_2$. The weight was then determined gravimetrically. Infrared spectra and boiling point (0 °C) determination of the crystalline liquid indicated the presence of pure $B(C_2H_5)_3$ in the tube.

An Advanced Kinetics model MIRL-50 grating tuned $CO_2$ laser was used to irradiate the gas samples. In all cases the laser was tuned to the P(20) line of the 10.6 μm transition (944.21 $cm^{-1}$). The power was 5.3 W and the intensity 13.8 $W/cm^2$. Beam diameter was 0.7 cm and irradiation times were always 2 s. No reaction ever occurred when the power of the laser was below 5 W.

## Results and Discussion

The infrared absorption spectrum of the mixture $B_2H_6$–$C_2H_4$ (1:6) prior to irradiation with the $CO_2$ laser is displayed in Fig. 1a. The spectrum of the mixture after irradiation is shown in Fig. 1b. It can be observed in this figure that the strong bands corresponding to $B_2H_6$ have disappeared (see Figs. 1a and 1b). Figure 3c corresponds to the spectra of the fraction collected at –95 °C. Clear features corresponding to the pure product $B(C_2H_5)_3$ are shown. All the bands in the spectra of Fig. 3c have been reported previously by W. J. Lehmann *et al.* [15] in a study of the characteristic frequencies of triethylborane. Absorption due to CH stretching frequencies in the 2800–2900 $cm^{-1}$ range, HCH bending frequencies around 1471 $cm^{-1}$, and B–C stretching frequency at 1120 $cm^{-1}$ confirm the presence of pure $B(C_2H_5)_3$.

Table I shows the initial pressures, composition, and total pressures of the mixtures of $B_2H_6$ and $C_2H_4$ before irradiation. Also listed in Table I are the pressure of unreacted $C_2H_4$ remaining in the cell, the pressure of $H_2$ formed, the mass of liquid $B(C_2H_5)_3$ and the percentage yield obtained for each composition after irradiation of the sample mixture. Upon examination of these data several trends are noticed. At fixed total pressure (320 Torr) of $B_2H_6$–$C_2H_4$ mixtures, the amount of polymeric material and $H_2$ increase as the mole fraction of $B_2H_6$ increases in the mixture. Several experiments were done using a 1:1 mixture which produced mainly $H_2$, polymeric material and small amounts of $B(C_2H_5)_3$. The situation is reversed when the mole fraction of $B_2H_6$ is decreased. For a $B_2H_6$–$C_2H_4$ (1:6) mixture, the product inside the cell is a yellowish liquid. After purification, a small amount of boron hydride polymer remained in the cell and crystalline liquid $B(C_2H_5)_3$ was obtained. For a mixture of composition 1:12 the product in the cell is a crystalline liquid with no visible signs of the polymer. If the composition is fixed (1:6), the yield of $B(C_2H_5)_3$

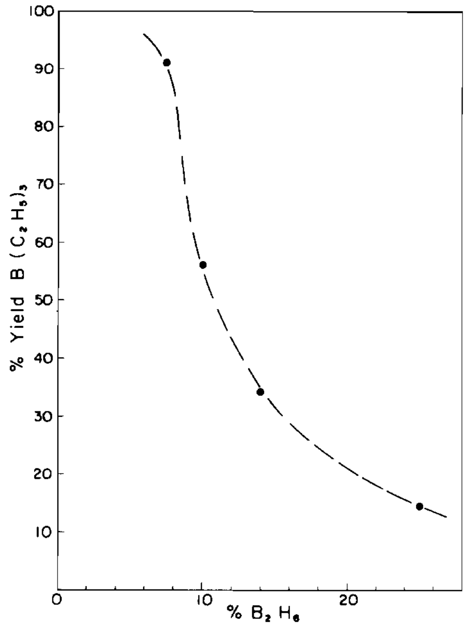

Fig. 2. Triethylborane percentage yield obtained after purification of the irradiated sample as a function of the percentage of $B_2H_6$ in the mixture $B_2H_6$–$C_2H_4$ before irradiation. Power was 5.3 W and intensity 13.8 W/cm$^2$. Irradiation time was 2 s. Total pressure 320 Torr.

is around 34% for a total pressure of 320 Torr. An increase in the total pressure to 455 Torr for a mixture of the same composition (1:6) results in a decrease (30%) of the yield of $B(C_2H_5)_3$. In Fig. 2 the percentage yield of $B(C_2H_5)_3$ is calculated from the number of moles of product obtained after purification and eqn. (1) is plotted as a function of the $B_2H_6$ mole fraction in the mixture before irradiation. A dramatic increase in the percentage yield of $B(C_2H_5)_3$ is obtained by decreasing the mole fraction of $B_2H_6$. In particular the 1:12 mixture produces a 91% yield with minimal formation of $H_2$ and traces of boron hydride polymer. Although the microscopic reaction is complex and out of the scope of this report, the results suggest that there is a competition between the following reactions:

$$B_2H_6 + 6C_2H_4 \xrightarrow{h\nu} 2B(C_2H_5)_3 \qquad (1)$$

$$(n/2)B_2H_6 \xrightarrow{h\nu} (BH)_n + nH_2 \qquad (2)$$

The formation of $B(C_2H_5)_3$ from reaction (1) of boron hydride polymer and $H_2$ from reaction (2) can be controlled by changing the composition of $B_2H_6$ in the mixture.

In summary, a convenient method of synthesis and purification of triethylborane from gaseous diborane and ethylene mixtures is reported. An infrared cw $CO_2$ laser was used to initiate a thermal explosion which results in high yields of the product in a very short reaction time.

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