1698 *Inorg. Chem.* **1981**, *20*, 1698–1701

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14853

Partial Reduction of Trimethoxyborane: An Old Reaction in a New Reactor

PETER M. JEFFERS and S. H. BAUER*

Received September 12, 1980

Forty–fifty percent conversion of trimethoxyborane to $HB(OCH_3)_2$ was achieved by passing $B(OCH_3)_3/H_2$ mixtures through a carefully controlled microwave discharge; almost all of the unconverted reactants were recovered. Similar but much less efficient reductions were obtained by exposing the reactants to focused pulses of CO_2 laser radiation [P(26)–P(34) lines of the 9.6-μm band]. We were not successful in reducing trimethoxyborane by activating these mixtures with electrical discharges, with continuous, unfocused laser radiation, or via Hg-photosensitized photolysis. No significant reductions were achieved by any mode of excitation when H_2S, NH_3, C_2H_2, or CH_4 replaced the H_2. However, the reaction $B(OCH_3)_3 + SiH_4 = HB(OCH_3)_2 + SiH_3(OCH_3)$ proceeds smoothly under CW laser irradiation.

Introduction

It was established many decades ago that only H_2, BeH_2, and $Be(BH_4)_2$ exceed diborane in the heat of combustion per gram. This led to a government-sponsored research program beginning about 1950, which had the goal of synthesizing high-energy fuels. In these investigations a variety of synthetic routes for B_2H_6 were developed,[1] but the cost of these "exotic" fuels remained high. Among the attractive diborane syntheses is the disproportionation of dimethoxyborane, $HB(OCH_3)_2$, to give B_2H_6 and $B(OCH_3)_3$, a reaction first pointed out by Burg and Schlesinger.[2] The rate parameters for this disproportionation (eq 1) were measured by Uchida and coworkers,[3] who found it to follow a clean but heterogeneous mechanism at temperatures from 40 to 80 °C, with a 14 kcal/mol activation energy.

$$6HB(OCH_3)_2 \rightleftarrows B_2H_6 + 4B(OCH_3)_3 \qquad (1)$$

The documented preparations of $HB(OCH_3)_2$ include (a) reduction of trimethoxyborane[4] or trimethoxyboroxine[5] with metal hydrides, borohydride, or alkoxyborohydride, (b) reaction of $B(OCH_3)_3/H_2$ mixtures in a flow tube at 950 °C,[6] and (c) reaction between B_2H_6 and CH_3OH.[2,3] The first method requires 2 days of refluxing and produces the dimethoxy compound in a yield of about 35%. When B_2O_3 was added to the trimethoxyborane and the reduction carried out with $NaBH_4$, the yield was 64% (based on the borohydride which was converted[5]). The reaction between $B(OCH_3)_3$ and $NaHB(OCH_3)_3$ (at 68 °C) gives $HB(OCH_3)_2$, which constitutes 67% of the distillate.[7] It is not surprising that with the hot-tube flow reactor (preparation b) one obtains a low yield (≈13%). The equilibrium constant for the direct reaction

$$B(OCH_3)_3 + H_2 = HB(OCH_3)_2 + CH_3OH \qquad (2)$$

is estimated to be 1.6×10^{-7} at 950 °C. Clearly a highly nonequilibrium condition exists in the rapid flow stream. Were the contact time long enough, both the dimethoxyborane and the methyl alcohol would pyrolyze at that temperature. Finally, in method c diborane is destroyed; this reaction is opposite to our synthetic objective.

Since trimethoxyborane is a low-cost, readily available material, we considered it worthwhile to test several techniques for energy deposition under nonequilibrium conditions in an attempt to reduce it. Here we report on experiments with CW and pulsed CO_2 lasers, electrical discharges, microwave discharges, and Hg-photosensitized photolysis. We investigated mixtures of $B(OCH_3)_3$ with a number of reducing agents, including H_2, C_2H_2, CH_4, CO, and H_2S, and did discover a promising synthetic route for $HB(OCH_3)_2$.

Microwave Discharge Experiments

A flow system was set up consisting of a 5-L "driver" bulb connected via a stopcock to a microwave-discharge region (in a Pyrex tube of 13- or 9-mm diameter) and then through a capillary flow restrictor to a series of U-traps (Figure 1a). The pressure in the "driver" bulb was carefully controlled; it could range up to 35 torr, limited by the fact that the glow discharge could not be maintained at higher pressures. The flow rate, controlled by the length and diameter of the capillary, is crucial; optimum results were obtained when the pressure drop was 4 torr/min at 20 torr driver pressure and when a total microwave power of about 20 W was maintained. Higher flow rates with lower power levels were not quite as effective. Control of the power levels is also critical, since too high a setting leads to extensive pyrolysis. The diameter of the flow tube in the discharge head was not critical, although the smaller diameter tubes allowed maintainance of the discharge at somewhat higher pressures and thus increased the yield per unit time.

Our best run was with 5% $B(OCH_3)_3$ in H_2, when the pressure dropped from 25.5 torr to 18 torr in 120 s; 54% conversion to $HB(OCH_3)_2$ was obtained, and we were able to recover almost all of the unconverted $B(OCH_3)_3$. A number of other runs gave conversions from 30 to 40% for mixtures varying from 0.7 to 10% $B(OCH_3)_3$ in H_2. The material accumulated from several "large-scale" runs [70–200 torr L of 10% $B(OCH_3)_3$ in H_2] was fractionated by trap-to-trap distillation. The most volatile fraction (−100 to −196 °C) contained C_2H_2 and C_2H_4, identified by mass and IR spectra. The large −85 to −110 °C fraction was $HB(OCH_3)_2$. Its IR spectrum matched that reported by Barton.[8] The −85 °C remnant was mostly $B(OCH_3)_3$.

We recorded the spectrum of the blue-gray light emitted by the discharge region. The H Balmer lines were evident, and a number of BO bands were present. No other features were definitely identified, although there were numerous lines and bands on the plate.

A number of IR spectra were taken with a cell wherein the sample could be deposited directly on a liquid-N_2-cooled window. Thus we obtained very clean low-temperature spectra of $HB(OCH_3)_2$ and were able to investigate the white solid usually found after the cold traps were warmed. The first scan (−196 °C) of the deposit generated in a 5% $B(OCH_3)_3/H_2$ reaction showed the $B(OCH_3)_3$ peaks, weak peaks of $HB(OCH_3)_2$, and a broad shallow absorption from 3000 to 3500 cm^{-1}. There was good discrimination between the $B(OCH_3)_3$

---

(1) See: "Boron, Metallo-Boron Compounds, and Boranes"; Adams, R. M., Ed.; Interscience: New York, 1969; Chapter 7.

(2) Burg, A.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1933**, *55*, 4020.

(3) Uchide, H. S.; et al. *J. Phys. Chem.* **1959**, *63*, 1414.

(4) Bush, J. D.; Carpenter, R. A.; Schechter, W. H. U.S. Patent 3 104 059, 1954; *Chem. Abstr.* **1962**, *56*, 8563.

(5) Bush, J. D. U.S. Patent 3 014 060, 1955; *Chem. Abstr.* **1962**, *56*, 8563.

(6) Edwards, L. J.; Pearson, R. K. U.S. Patent 3 205 255, 1965; *Chem. Abstr.* **1966**, *64*, 596.

(7) French Patent 1 306 638, 1962, assigned to Callery Co. (*Chem. Abstr.* **1963**, *58*, 8906).

(8) Barton, L. "Gmelins Handbuch der Anorganischen Chemie"; Verlag Chemie: Weinheim/Bergstr., 1977; Vol. 48, Part 16, p 1.

0020-1669/81/1320-1698$01.25/0

Table I

discharge mixture	post-feed	dist of nozzle from discharge, cm	results
10% $B(OCH_3)_3$ in H_2	C_2H_2	5	no reaction involving C_2H_2
10% $B(OCH_3)_3$ in H_2	C_2H_2	2–4	C_2H_2 pyrolysis products
10% $B(OCH_3)_3$ in Ar	C_2H_2	1–3	extensive pyrolysis [loss of $B(OCH_3)_3$]; C_4H_2, C_2H_4, some benzene, and toluene generated
2% $B(OCH_3)_3$ in Ar (air contamination)	H_2	2.5	efficient production of HCN
2% $B(OCH_3)_3$ in Ar	H_2	3	C_2H_2 produced; most $B(OCH_3)_3$ destroyed
10% $B(OCH_3)_3$ in CO	none		C_2H_2 and CO_2 formed; most $B(OCH_3)_3$ destroyed
10% $B(OCH_3)_3$ in He	none		C_2H_2 and C_2H_4 formed but not as much $B(OCH_3)_3$ pyrolysis as with CO
10% $B(OCH_3)_3$ in He	H_2	1–3	C_2H_2 and C_2H_4 formed; some conversion to $HB(OCH_3)_2$
10% $B(OCH_3)_3$ in He	C_2H_2	1	C_4H_2 formed; slight $HB(OCH_3)_2$ production
10% $B(OCH_3)_3$ in He	H_2S	1	C_2H_2; major product CS_2
10% $B(OCH_3)_3$ in He	D_2	1	extensive isotopic scrambling

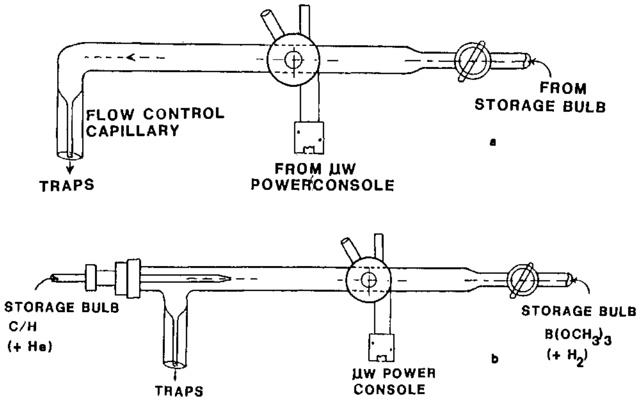

Figure 1. (a) Schematic of microwave-discharge flow reactor. (b) Configuration for postdischarge injection of reducing agent.

bands at 1360 and 1500 cm^{-1}. After the cell was warmed for 30 min, a second scan showed no $B(OCH_3)_3$ bands, and the spectrum was a good match for $B(OH)_3$, with the 1360- and 1500-cm^{-1} peaks essentially fused; absorption at 3200 cm^{-1} actually increased over the first scan. The cell was warmed and pumped overnight, after which a final scan showed no absorption.

Hydrocarbons as Reducing Agents

The possibility that carboranes might be formed from MW-generated fragments of $B(OCH_3)_3$ and various hydrocarbons led us to test a mixture of 10% $B(OCH_3)_3$ in CH_4. The character of the discharge was much like that for H_2 mixes, but conversion to $HB(OCH_3)_2$ was very small, and no new H/B/C/O or H/B/C compounds were found. The mass spectra did indicate that C_2, C_3, and C_4 hydrocarbons were present. A white deposit appeared at the entrance to the liquid-N_2 trap which slowly disappeared upon standing at room temperature.

The discharge was very difficult to maintain in a mixture of 13% $B(OCH_3)_3$ in C_2H_2, even at 5 torr; an operating Tesla coil had to be kept close to the tube to sustain the blue glow. In these experiments the discharge tube was rapidly coated with a dark deposit. Several runs were also made with pure C_2H_2, and the products in both cases yielded mass spectral peaks which ranged in m/e almost continuously from 24 through 110. The components identified among this wealth of m/e peaks included C_2H_6, C_4H_2, C_6H_2, benzene, toluene, and phenylacetylene. The only unique peaks found in the $B(OCH_3)_3$ system appeared at m/e 96, 97 which correspond to $H—C{\equiv}C—B(OCH_3)_2$, but these peaks were always small and no conditions were found which increased this conversion. Some $HB(OCH_3)_2$ may have been produced, but the yield did not approach that of the H_2 mixture nor its cleanliness of operation. The mass spectra for all the discharge experiments were regularly extended to $m/e = 200$, but no conclusive evidence was found to suggest formation of diboron species such as $B_2(OCH_3)_4$.

A final attempt to generate carboranes was made by altering the flow system (Figure 1b) so that the reactant gas was injected into the flow at a point beyond the discharge. A sliding seal allowed a nozzle tip to be positioned from 0 to 5 cm beyond the glow region. Pressures in the 5-L driver bulb and the 2-L postdischarge feed bulb were adjusted to be equal at the start of a run. The flow-restricting capillary was placed beyond the postfeed nozzle to allow for thorough mixing of the two streams. The results of this group of experiments are presented in Table I.

Electrical Discharge Experiments

No reaction occurred in a 3% $B(OCH_3)_3$ in H_2 mixture when subjected to an "electrodeless" discharge (a Tesla coil in contact with the center of a 1 cm × 30 cm Pyrex tube that had ground wires wound around each end) when the total pressure exceeded 60 torr. Significant coversion was found at total pressures of 3–50 torr for discharge durations of 15–30 s. The reaction appeared somewhat different from that induced by a focused laser beam (see below). Considerable amounts of H_2O ($m/e = 18$) and CO_2 ($m/e = 44$) were generated, and it was difficult to find conditions where most of the $B(OCH_3)_3$ was not destroyed. Small conversions to $HB(OCH_3)_2$ did occur, but the yields were not reproducible. This is consistent with the reported reduction of trimethoxyborane in a glow discharge.[9] Although many reports were published on the interconversion of boranes via glow discharges,[10,11] no practical synthetic routes appear to have been developed. Indeed, we found that the efficiency of conversion depends *sensitively* on pressures, flow rates, and specifics of the discharge such as frequency and power, mixture composition, etc., which must be controlled with great care.

Laser Experiments

In this laboratory we developed the LPHP technique,[12] i.e., the use of CO_2 lasers to power homogeneous pyrolysis, to induce laser-augmented decompositions[13] and to initiate detonations.[14] We noted the fact that ν_{21} (e′) of trimethoxyborane strongly absorbs the P(26)–P(34) lines of the 9.6-μm CO_2 laser band and anticipated that mixtures of $B(OCH_3)_3$

---

(9) Manior, J. P.; Frillici, F. V.; Preston, E. Report OMCC-HEF-91 submitted to the Olin-Matheson Chemical Corp., Nov 22, 1967, under Contract AF 33(600)-33920.

(10) Jolly, W. M. *Adv. Chem. Ser.* **1969**, *No. 80*, 156.

(11) Flinn, J. E.; Goldberger, W. M. *Adv. Chem. Ser.* **1969**, *No. 80*, 447–449.

(12) Shaub, W.; Bauer, S. H. *Int. J. Chem. Kinet.* **1975**, *7*, 509.

(13) Chien, K.-R.; Bauer, S. H. *J. Phys. Chem.* **1976**, *80*, 1405.

(14) Bauer, S. H.; Haberman, J. A. *IEEE J. Quantum Electron.* **1978**, *QE-14*, 233.

with various reducing agents may react when subjected to intense pulses of IR radiation. We used two distinct procedures: (A) thermal cycling at moderate total pressures (5–150 torr) using CW irradiation[15] and (B) repetitive, focused pulses (0.2–1.5-μs duration) at low and moderate pressures. In all of our experiments the radiation was line-selected for the optimum photolyzing frequency (which was to the red of the absorption maximum). In several of the A experiments a little SF_6 was added ($\approx$0.5–1.0 torr) to maximize the central core temperature. Most of the A experiments were performed with substantial levels of added Ar (10–100 torr). Under these conditions convection plays a dominant role for establishing the steady-state temperature in vertically heated cells of linear dimensions $\approx$10 cm.

The following briefly summarizes our observations on the copyrolysis of $B(OCH_3)_3$ with various reagents. No reactions were observed with H_2, NH_3, or H_2S. In $B(OCH_3)_3/C_2H_2$ mixtures, both species decreased in concentration, and the following products were identified: CH_4, CO, C_6H_6, C_2H_4, CH_3OH. No volatile boron-containing compound was generated, but solid residues were deposited on the cell walls and windows. Mixtures of trimethoxyborane and methylacetylene gave similar products with slightly different product distributions. When SF_6 was added and the mixture irradiated with the P(16) of the 10.6-μm band, higher temperatures were obtained. A solid boron-bearing species was identified as B_2O_3, along with the same volatile products. Acetylene only, with SF_6 as the heat-transfer agent, gives high levels of benzene and a little ethylene. Our results indicate that in the trimethoxyborane/acetylene mixtures the species pyrolyze individually, with no significant interaction of the intermediates, which must be short-lived indeed at the high temperatures required to fragment the trimethoxyborane.

Irradiation of trimethoxyborane and silane mixtures gave a relatively clean-cut exchange:

$$B(OCH_3)_3 + SiH_4 \rightarrow HB(OCH_3)_2 + H_3Si(OCH_3)_3 \quad (3)$$

We could not exclude the possibility that small amounts of $H_2Si(OCH_3)_2$ and $HSi(OCH_3)_3$ were also generated. The absence of B_2H_6 in the products indicates that $H_2B(OCH_3)$ was not produced, since it is unstable and disproportionates to $HB(OCH_3)_2$ and B_2H_6. The kinetics of this exchange reaction remains to be investigated. We also tested for a possible ligand exchange in the reaction between trimethoxyborane and tetramethylsilane; no new products were formed.

The multiphoton decomposition of $B(OCH_3)_3$ was achieved with pulsed CO_2 radiation (B experiments). The laser was tuned to the P(26) line of the 9.6-μm band and provided about 4 J/pulse of 200-ns duration. When the 1.5-cm diameter beam was *not* focused, there was essentially complete energy absorption within a 30-cm gas cell containing 1% $B(OCH_3)_3$ in CO or in H_2 at total pressures of about 300 torr, but there was no visible light emission. Analysis by IR and mass spectra showed that no reaction had occurred.

For the subsequent experiments we inserted a 20-cm focal length lens to focus the laser beam near the center of the gas cell. The samples were irradiated with 30–400 pulses, at a rate of 10–12 pulses/min. Pure $B(OCH_3)_3$ and 10% $B(OCH_3)_3$ in Ar or in CO, at total pressures of 15–600 torr, emitted a white, sparklike flash with each laser pulse; IR analysis showed a decrease in the $B(OCH_3)_3$ concentration, with C_2H_2 as the major gaseous product. Pulsed irradiation of 1–5% $B(OCH_3)_3$ in H_2 was also accompanied by visible light emission, but the color was purplish rather than white. Photographs of the visible light resolved by a 0.7-m prism spectrograph showed numerous lines and bands, although the only unambiguously identified features were the hydrogen Balmer lines, which were very strong and accounted for the observed color.

Products formed in the $B(OCH_3)_3/H_2$ mixtures include C_2H_2, C_2H_4, CH_3OH, and CH_4; these were identified by their IR and mass spectra. Quantitative mass spectrometry indicated as much as 25% conversion to $HB(OCH_3)_2$ had occurred, with 50% recovery of the original $B(OCH_3)_3$. The amount of trimethoxyborane converted or pyrolyzed varied approximately linearly with the number of pulses absorbed. With 300 pulses into 42 cm of a 3% mixture, nearly complete destruction of both $B(OCH_3)_3$ and $HB(OCH_3)_2$ was observed; then large amounts of C_2H_2 were generated.

One mixture of 5% $B(OCH_3)_3$ in D_2 subjected to 150 pulses showed some isotopic substitution both in the remaining trimethoxyborane and in the dimethoxyborane, but the most striking observation was that C_2D_2 (m/e = 28) was a major product while C_2H_2 (m/e = 26) was negligible. When mixtures (1:2) of $B(OCH_3)_3$ with C_2H_2 and H_2S were irradiated, no significant differences in product distribution were observed. The indications are that the radicals generated during the purplish flash react rapidly with each other and the partially excited trimethoxyborane prior to their encounters with the admixed species. Tests with $B(OCH_3)_3/H_2S \approx 1/10$ also showed no new compounds.

During the course of these laser experiments, parts of the gas-handling vacuum system became coated with a white solid deposit, which was not identified. The walls of the gas-irradiating cell also accumulated a similar white deposit, suspected to be B_2O_3.

Mercury Photosensitization Experiments

The appearance of the H Balmer lines in the emission from laser-pulsed $B(OCH_3)_3/H_2$ mixtures suggested that H atoms may play a significant role in the primary reaction sequence. We tested this hypothesis by irradiating a 10% $B(OCH_3)_3$ in H_2 mixture, saturated with Hg vapor, with λ 2537 nm from a low-pressure mercury lamp (500 W) using the apparatus described by Kline and Porter.[16] Irradiation of a 70 torr sample for over a 2 h showed no significant conversion. We conclude that H atoms are insufficiently reactive toward $B(OCH_3)_3$ to break into the very stable BO_3 unit.

Discussion

In the microwave-flow reactor, for a pressure drop of 3.75 torr/min in the 5-L driver bulb, using a mixture of 5% $B(OCH_3)_3$ in H_2, *at 40% conversion*, one calculates a production rate of 0.1 g of $HB(OCH_3)_2$/h. Our experiments indicated that both the flow rate and reactant concentration could be increased without significantly decreasing the extent of conversion. With optimized conditions one should be able to generate several tenths of a gram of $HB(OCH_3)_2$ per hour in a single reactor tube, and the entire process could be amplified by use of parallel reactor tubes, so that the production rate may compare favorably with the hydride reduction methods,[4,5] which require 1–2-day preparations. If the objective is the production of diborane, the methyl alcohol can be condensed and the $HB(OCH_3)_2/B(OCH_3)_3$ mixture injected directly into the disproportionation oven.[3] Then, the unconverted plus regenerated trimethoxyborane can be returned directly to the microwave flow-tube reactor.

Our experiments indicate that reaction occurred by recombination of molecular fragments produced in the plasma generated by either focused laser radiation or the microwave discharge. We call attention to the marked differences in reaction character between the controlled microwave and the

---

[15] Work performed by Dr. Hermann Fusstetter.

[16] Kline, G. A.; Porter, R. F. *Inorg. Chem.* **1977**, *16*, 11.

other forms of electrical discharges. Such dissimilarities have been pointed out by Blaustein and Fu[17] as well as by Wightman and Johnson.[18] However, Frazer and Holzman[19] did obtain yields of B_2Cl_4 with microwave excitation of BCl_3 similar to those reported by Urry, Wartik, Moore, and Schlesinger,[20] who used an electrical discharge.

Since no reduction was observed in the mercury photosensitization experiments, H atom attack on undissociated $B(OCH_3)_3$ cannot be an important step in a mechanistic scheme for the generation of $HB(OCH_3)_2$. Note that H atoms were present in both the laser- and microwave-driven systems, as indicated by the recorded Balmer lines and the considerable isotopic scrambling found with D_2 mixtures such as the production of C_2D_2 in $B(OCH_3)_3/D_2$. That carbon atoms were present in the postdischarge stream was indicated by the experiments wherein H_2S was used as the reducing agent; the major product was CS_2. Grimes[21] reported the production of carboranes in electrical discharges through B_2H_6/C_2H_2 mixtures, but he obtained less than 5% yields of volatile products. Small amounts of carboranes may have been produced in our microwave discharges, but this is not an efficient route for generating high yields of these desirable materials.

The results summarized in Table I indicate that the molecular fragments produced within the discharge region lived long enough to travel several centimeters down the flow tube. We found that CH_4, C_2H_2, and H_2S were pyrolyzed when these reagents were injected into the flow system as far as 4 cm beyond the discharge. With this configuration the pyrolysis was much cleaner (especially of C_2H_2) than it was when the gases passed directly through the discharge. An interesting observation was that He provided a considerably more moderate environment than did Ar; under similar flow and power conditions $B(OCH_3)_3$ was much more extensively pyrolyzed in Ar than in the He mixtures.

$$B(OCH_3)_3 \xrightarrow[\text{discharge}]{(e)} B(OCH_3)_2 + CH_3O \tag{4}$$

$$\xrightarrow{(e)} OB(OCH_3)_2 + CH_3 \tag{5}$$

$$H_2 \xrightarrow{(e)} 2H \tag{6}$$

$$B(OCH_3)_2 + \left\{\begin{matrix} H_2 \\ H \end{matrix}\right. \longrightarrow HB(OCH_3)_2 + H \tag{7}$$

$$CH_3O + \left\{\begin{matrix} H_2 \\ H \end{matrix}\right. \xrightarrow[(M)]{} CH_3OH + H \tag{8}$$

$$OB(OCH_3)_2 + \left\{\begin{matrix} H_2 \\ H \end{matrix}\right. \longrightarrow HOB(OCH_3)_2 + H \tag{9}$$

$$OB(OCH_3)_2 \longrightarrow \cdots BO \xrightarrow{(wall)} B_2O_3 \tag{10}$$

$$6HOB(OCH_3)_2 \xrightarrow{(wall)} 2B(OH)_3 + 4B(OCH_3)_3 \tag{11}$$

$$H + H \xrightarrow[(wall)]{(M)} H_2 \tag{12}$$

The sequence (4)–(12) is a *minimal* set with which we can account for most of our observations. Equation 4 followed by (7) and (8) lead to the major products, while the alternate primary process, rupture of C–O bonds in (5), is followed by (9) and (11); in the cold traps sequence 10 occurs. The branching ratio between (4) and (5) was optimized in our experiments. Apparently, the disproportionation (11) proceeds more readily than does the corresponding reaction for $HB(OCH_3)_2$. We did observe the direct formation of $B(OH)_3$ upon warming of the cold window, but we did not find evidence for B_2H_6 via IR or mass spectra. Emissions from excited states of BO and H arise from electron–fragment collisions in the plasma. From among the numerous fragment recombination reactions which could occur, only the species stable at elevated temperatures emerge, i.e., C_2D_2, C_2H_2, and CS_2. The presence of atomic hydrogen readily explains the extensive isotopic scrambling in D_2 mixtures. These also can serve to initiate the usual chain processes involved in the pyrolysis of CH_4 and C_2H_2, which did occur when the latter were added to the flow beyond the discharge zone.

As a final note, there are some interesting differences between our findings and those reported by Edwards and Pearson.[6] They implied that an electric discharge can be used as effectively as a heated tube; we found that an electric discharge was much less efficient than a microwave discharge. They also reported better reduction of $B(OCH_3)_3$ with CO or CH_4 while we found H_2 very efficient whereas both CO and CH_4 were ineffective. CO had a decidedly negative influence on the microwave discharge while CH_4 appeared to undergo parallel pyrolysis, with little interaction of its fragments with the trimethoxyborane.

Acknowledgment. This work was supported by the ARO under Grant No. DAA G29-76-G-0327. We thank Professor R. F. Porter for helpful suggestions regarding use of the photolysis apparatus and the cryogenic-window IR cell. We sincerely acknowledge the extensive work done by Dr. Hermann Fusstetter, who further developed the LPHP technique and a flow-through pyrolysis cell. He discovered eq 3.

Registry No. $B(OCH_3)_3$, 121-43-7; $HB(OCH_3)_2$, 4542-61-4; SiH_4, 7803-62-5.

---

(17) Blaustein, B. D.; Fu, Y. C., *Adv. Chem. Ser.* **1969**, *No. 80*, 259.

(18) Wightman, J. P.; Johnson, N. J. *Adv. Chem. Ser.* **1969**, *No. 80*, 322.

(19) Frazer, J. W.; Holzman, R. T. *J. Am. Chem. Soc.* **1958**, *80*, 2907.

(20) Urry, G.; Wartik, T.; Moore, R. E.; Scheslinger, H. I. *J. Am. Chem. Soc.* **1954**, *76*, 5293.

(21) Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 1895.