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# Hydrogen atom abstraction by O(3P) from diborane and ethane

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We measured, via LIF, time-dependent concentrations of OH resulting from the reaction of  $O({}^{3}P)$  with  $B_{2}H_{6}$  and  $C_{2}H_{6}$ . The oxygen atoms were generated by titrating microwave discharged  $N_{2}$ /He with NO to the chemiluminescent end point. The operating pressures in the flow reactor ranged from 5 to 15 Torr; the mixtures consisted of  $He/O({}^{3}P)$ /fuel in the approximate ratios 100/1/0.1 to 100/1/1. Flow conditions were such that in the low pressure experiments the controlled residence time prior to detection were 0.8-17 ms; under the higher pressure conditions, the time interval covered was 2-35 ms. We estimated that the temperature of the reaction region was  $\approx 350$  K, based on rotational emission temperatures measured for BO\*, generated under closely similar conditions. First a complete mechanism was derived for ethane for a specified set of experimental parameters. For ethane, a single set of experimental conditions was selected for ratioing the recorded intensity to the computed OH density; this was cross checked with other runs for ethane. Finally, a mechanism was developed for  $B_{2}H_{6}$ , which quantitatively checked our experimentally determined profiles both in shape and magnitude, for three sets of conditions, and within a factor of 2 for the high concentration runs (100%  $B_{2}H_{6}$  feeding into the reactor at 14 Torr).

## INTRODUCTION

The common characteristics of oxidations of boron hydrides and related compounds are rapid rates, large exothermicities, and strong visible and ultraviolet chemiluminescence. These features lead to the expectation that the reaction may generate products in nonthermal distributions, and possibly could be used to construct chemical lasers at visible wavelengths. General reviews of reactions between molecular oxygen and diborane date back to reports by Berl<sup>1</sup> and by Bauer and Wiberley<sup>2</sup>. The reaction between diborane and atomic oxygen was initially studied by Hand and Derr<sup>3</sup> in a flow-tube reactor. More recently, Anderson and Bauer<sup>4</sup> measured the rates of attack of  $B_2H_6$  and  $H_3BCO$  by O and N atoms under rapid-mixing fast-flow conditions, using direct sampling by a TOF mass spectrometer. The dynamics of reaction between oxygen atoms and borane trimethylamine, based on spectral analysis of the chemiluminescence were described by Jeffers and Bauer.<sup>5,6</sup> Although considerable information is available on the chemistry of boranes,<sup>7</sup> the complex mechanism operating during O atom attack, other than the total rate of destruction of the borane, has not been formulated except in a theoretical paper by Shaub and Lin.<sup>8</sup>

The importance of fully characterizing the reactions of fuels with  $O({}^{3}P)$  and with  $OH({}^{2}\Pi_{i})$  can be judged from the vast literature on these reactions which has accumulated during the past fifteen years. For oxygen-atom attack on alkanes a current summary has been prepared by Cohen.<sup>9</sup> Earlier reviews were assembled by Herron and Huie.<sup>10</sup> There is total agreement that the primary products are alkyl radicals and OH. The vibrational state distribution of the hydroxyl radicals increases in the sequence: primary  $\rightarrow$  secondary  $\rightarrow$  tertiary (as do the corresponding exo-

thermicities), whereas the rotational state distribution appears to be independent of the type of hydrogen which has been abstracted,<sup>11</sup> with relatively little energy deposited in rotation. These observations are consistent with a collinear "three atom" model [R–H–O] for the transition structure.<sup>12</sup> The energies of activation range from 7.3 kcal/mol for straight chain primary H's to 2.5 kcal/mol for tertiary H's; the entropies of activation (298 K) span the interval – 19.2 to -22.7 e.u., depending on the number and types of hydrogens present. Typically  $k(298) \approx 10^{11} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$ .

The abstraction of H atoms from alkanes by OH radicals follows a similar pattern. An extended review was prepared by Atkinson *et al.*<sup>13</sup> about seven years ago. Cohen's significant procedure for extrapolating the available experimental data to higher temperatures<sup>14</sup> (as required for combustion applications) was recently implemented by Walker<sup>15</sup> for the range 300–1000 K. The entropies of activation are generally higher than for oxygen atom attack (-23 to -27 e.u.), but the rate constants are larger, typically  $k(298) \approx 10^{12.5}$  mol<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>. These are comparable to rate constants for the gas phase abstraction of hydrogens by chlorine atoms.<sup>16</sup>

A general feature of the kinetic measurements is that they were made under conditions in which one species was present in large excess over the other, so as to minimize complications due to secondary reactions. Recently, however, it has been pointed out by Cohen<sup>17</sup> that in alkane +  $O({}^{3}P)$ reactions, the measured values are particularly sensitive to errors introduced by uncounted secondary reactions and by low levels of impurities. Detailed discussions of chemical kinetic modeling of hydrocarbon oxidation under combustion conditions were reviewed by Westbrook and Dryer.<sup>18</sup>

It is evident that until rates of *production* of specific species are determined, overall mechanisms cannot be established. In this report we present time-dependent OH concentrations generated under a variety of initial conditions, upon mixing excess  $O({}^{3}P)$  with diborane, based on the reaction

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 $[C_2H_6 + O(^{3}P)]$  for calibration of our experimental protocol. The products of a fast-flow reactor were sampled via LIF by OH. Dutton et al.<sup>19</sup> adopted the LIF technique for determining dynamics of the OH produced in molecular beams, for the abstraction from hydrocarbons, cyclic hydrocarbons, and ethanol. Their observations indicated that the abstraction is a direct step and takes place only when the oxygen atom is collinear with the C-H bond under attack. In our experiments OH( $A^{2}\Sigma^{+} - X^{2}\Pi_{i}$ ) fluorescence intensities for all runs were measured under strictly comparable conditions and reduced to absolute OH concentrations by ratioing the computed value to the measured fluorescence intensity at a single experimental point from an extended run for  $C_2H_6$ , assuming that the proposed mechanism for ethane is quantitatively correct. The internal consistency of this assumption is demonstrated below. Computational simulations were developed, and the time-dependent concentrations were compared with the experimental values. Thus, we derived the "best" estimates for the rate coefficients at the temperature of the flow medium, which is in the vicinity of 350 K, based on the rotational temperature determined in a similar flow system.6

## **EXPERIMENTAL**

Figure 1 is a schematic of the apparatus. It consists of a microwave discharge arm, a flow reactor, and a detection

chamber. The reactor is a Pyrex tube 2.5 cm in diameter (upper part) and 1.25 cm (lower part), with a 30 cm long reaction zone. Atomic species are generated in a microwave discharge and injected into the reaction zone through the side arm, as indicated. Samples of fuel are introduced through a 0.63 cm i.d. Pyrex tube, which can be slid along the axis of the reactor to displace the mixing region relative to the sampling pinhole. The reactor is evacuated by a fast mechanical pump; the pressure in the reactor can be controlled and maintained at 1-15 Torr, depending on the opening of the valve. The sampling pinhole is 0.50 mm. That section of the apparatus was constructed following the design developed by Anderson and Bauer.<sup>4</sup> The reactions products expand under near-continuum flow through the skimmer into the detection region. With this configuration the molecular densities measured are the concentrations developed along the central streamline. The stainless steel detection chamber is evacuated by a 10 cm oil diffusion pump; the background pressure in the detection area is maintained at  $< 10^{-3}$  Torr.

The hydroxyl radicals are detected by laser induced fluorescence of OH  $[A^2\Sigma \leftarrow X^2\Pi]$  at the (0,0) band, for the  $Q_1$  (1) transition (307.9 nm). A Nd:YAG laser (Quanta-Ray DCR), operating at a repetition rate of 10 Hz, pumps a Quanta-Ray PDL-1 pulsed dye laser (sulforhodamin 101). Its output is frequency doubled with a KDP crystal (Quanta-Ray crystal module-1) to produce a maximum pulse ener-



FIG. 1. Schematic of apparatus.

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gy of about 1 mJ at 308 nm and a bandwidth of  $\approx 0.1$  nm FWHM. The laser beam passes through a visible light rejection filter, an iris, and through a lens which focuses it onto the well-defined jet that emerges from the skimmer. The entrance and exit quartz windows are set at the Brewster angle. To minimize scattered laser light a series of baffles were inserted in long arms, and the walls of the vacuum chamber were painted black. On exit a portion of the direct beam is monitored with a photomultiplier. The fluorescence signal is detected by a EMI 6256B photomultiplier set at right angles with respect to both the directions of the laser beam and the jet. A filter (Hoya 4340) was mounted in front of the photomultiplier to reject wavelengths outside the region 275-375 nm. Initially the output of a boxcar integrator, operating with a gate width of 5  $\mu$ s, was recorded and averaged graphically. However, the incorporated background levels comprised the major part of the signal. More reliable data are obtained (as indicated in Fig. 1) with a Biomation digitizer (10 ns/pt) reading into a dual channel Tracor-Northern, which is set to subtract the background profile (recorded immediately prior to each run) from the fluorescence profile. The first  $\approx 100$  ns of the scattered light signal are not recorded. The exponential decay curve from OH(A  ${}^{2}\Sigma^{+}$ ) is plotted and digitally integrated to generate a single point for each combination of experimental parameters.

Ground state oxygen atoms are produced by visual titration with NO of discharged  $(N_2 + He)$ , which passes through the microwave cavity; this yields a stream of O atoms free of O<sub>2</sub>. The rates of the gas flow are monitored by a series of metering valves and flow meters, which were calibrated by measuring the rates of pressure decrease in known volumes. Under typical experimental condition, the flow rates of the gases are:  $1.43 \,\mu$ mol/s (for C<sub>2</sub>H<sub>6</sub>),  $3.62 \,\mu$ mol/s (for NO), 196  $\mu$ mol/s (for N<sub>2</sub>), and 336  $\mu$ mol/s (for He), at a flow reactor pressure (total) of 7 Torr. The linear flow speed of the sample was calculated to be  $2.1 \times 10^3$  cm/s, so that the shortest dwell time in the reactor is about 0.8 ms; the longest time can be extended to  $\approx 17$  ms for reactor pressure at 7 Torr, and to 35 ms at 14 Torr.

The stock gases used in these studies were obtained from AIRCO for  $N_2$  (99.995%), He (99.995%), and Ar (99.998%), and from Matheson for NO (cp, 99.0% min). This gas was purified by trap-to-trap distillation prior to use. To check for impurities in  $C_2H_6$ , the gas was injected onto an FID gas chromatograph (F&M Scientific Co., model 810) with a GC column consisting of 20% carbowax 20 M on 100/120 supelcoport. The total impurity level was found to be less than one part per thousand (<0.1%). Diborane was prepared by the action of 85% phosphoric acid on NaBH<sub>4</sub>. It was separated from other products (mostly H<sub>2</sub> and  $Na_3PO_4$ ) by successive distillation, and collected in a  $LN_2$ trap. The FTIR spectrum of diborane purified by this procedure showed no impurities. The  $B_2H_6$  was stored at - 196 °C and redistilled immediately before use. Vapors of the fuels were mixed with He (baromatic mixing) to obtain the desired concentrations. In contrast to data sets recorded with ethane, which were highly reproducible, runs with diborane showed irreproducibilities (  $\pm 20\%$  ). These fluctuations were minimized by careful cleaning and drying of the flow-reactor tube every 3-5 runs.

An intense blue chemiluminescence was observed with diborane, due to the formation of BO<sup>\*</sup>.<sup>4,5</sup> Its intensity increased with the concentration of the hydride. This cool blue emission consists of BO- $\alpha$  bands ( $A^{2}\Pi \rightarrow X^{2}\Sigma^{+}$ ), and is generated by the reaction of oxygen atoms with BH, and possibly with BH<sub>2</sub>.<sup>5,6</sup>

# EXPERIMENTAL PROCEDURES; INTENSITY CALIBRATION

When the dye laser output was scanned over a 0.3 nm on either side of 307.9 nm, fluorescence from OH, generated by reaction between the fuel and  $O({}^{3}P)$ , appears as sharp line features, assigned to  $Q_1(1)$  at 307.93;  $Q_1(2)$  at 308.09 nm. The recorded intensity developed at a selected transition can be changed by rotating the doubling KDP crystal to maximize the laser power at the desired resonance frequency. In view of the constant low levels of exciting radiation quenching effects are negligible. Intensities were recorded for different positions of the injecting tube to develop temporal profiles of OH concentrations. For each fuel several sets of experiments were performed at two total pressures, set at 7 or 14 Torr. The pressure in the reactor was varied by changing the aperture of the valve which connects the reactor tube to the mechanical pump, so that concentrations of the sample and of the oxygen atoms were changed by the same amount. C<sub>2</sub>H<sub>6</sub> shows a linear increase with pressure, as expected for a bimolecular reaction with a modest rate constant; also  $B_2H_6$  was demonstrated to show a linear response to flow rate.

The following strategy was developed to obtain a quantitative relation between the magnitudes of integrated fluorescence signals and the corresponding concentrations of OH (mol  $1^{-1}$ ) at the intersection of the laser beam with the jet, which samples the central stream within the flow reactor.

(a) A set of reactions and rate constants (at 350 K) for  $[C_2H_6 + O({}^{3}P)]$  were assumed, based on numerous literature reports. These were slightly adjusted (see below) until the computed [OH], coincided with the observed profiles, and precisely scaled with operating pressure and reactant concentrations (Fig. 2).

(b) For a selected set of experimental conditions three computed points were identified with corresponding signal levels, and their ratio averaged, thus providing a factor that relates [OH] to the recorded signal.

(c) Immediately before and directly after a run with another fuel, reference runs with ethane were recorded, with all experimental parameters such as laser intensity, flow rates, and operating pressures kept constant.

(d) In view of the comparable levels of incident laser intensity and recorded fluorescence for  $C_2H_6$  and  $B_2H_6$ , small saturation effects, if present, cancel.

## **DETAILS OF MECHANISM**

A general kinetics code developed at NBS<sup>20</sup> was expanded by Dr. N.-S. Chiu in several respects. The program requires only that the reacting species be specified, their reactions listed, and for each a rate constant inserted (for a fixed

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FIG. 2. [OH] observed (O and O) and calculated via the mechanism listed in Table I (350 K).

temperature run). One then obtains a printout of: (a) the concentration of each of the species as a function of time; (b) the rates of each reaction as a function of time; (c) the Jacobian for any selected species relative to all the others at selected (prespecified) times; in our case,  $d\{\partial[OH]/\partial t\}/d[X]$ . These provide direct measures of the sensitivity of the species of interest to inclusions of other species and of plausible reactions. 50 species and 200 reaction rates can be integrated.

The calculations were carried out to simulate our experimental parameters. A set of 67 of the most plausible reactions needed to describe the evolution of the systems  $O({}^{3}P)$  with  $C_2H_6$  were used. The initial concentrations of the reactants were calculated from measured flow rates. These ranged from  $8.3 \times 10^{-7}$  to  $3.2 \times 10^{-6}$  mol/ $\ell$  for ethane and  $1.4 \times 10^{-6}$  to  $1.7 \times 10^{-6}$  mol/ $\ell$  for oxygen atoms, with total pressures 7 to 14 Torr. Note that in the reactor the major constituent was helium (at about  $3 \times 10^{-4}$  mol/ $\ell$ ) so that the reactants were present at roughly 1/100 of that level.

Under our experimental conditions, the initial abstraction step

$$O + C_2 H_6 \rightarrow C_2 H_5 + OH$$

is rapidly followed by many secondary and tertiary processes. A model consisting of 30 species, participating in 67 reactions, was assembled and integrated to generate the OH concentration profiles. It soon became evident that only 16 species were essential and the number of reactions was reduced to 29, presented in Table I. Winnowing was achieved by carefully examining the computer outputs. We found that the concentration of each species at corresponding time scales were within 10% of those calculated with the larger set (67 reactions). It is significant to note that at low temperatures 13 reactions (3 to 15) appear in all H/O systems. The time-dependent concentrations of OH are very sensitive to these rate constants. Since they are present in all low pressure and low temperature flames for hydrogenic fuels these 13 reactions were incorporated (unaltered) in every mechanism, as listed in Table I.

The rate constants used in the simulations were selected primarily from Refs. 21 and 22. A few of the rate constants were estimated from analogous reactions. Several were subjected to reasonable revisions, required to obtain fits between the computed and absolute magnitudes, as well as the time dependent-OH concentrations, with those observed. For three-body reactions [3, 5, 6, 7, 9, 10, and 11] corresponding two-body rate constants were obtained by multiplying the three-body values by the concentration of M at the corresponding reactor pressure. Also, since there are no ambient temperature values available for reactions 5, 6, and 9, we inserted somewhat larger values than those reported for high temperatures. This is justified in view of the demonstrated negative temperature dependence ( $T^{-1}$  to  $T^{-1.5}$ ) for termolecular associations with small or zero activation energies.<sup>23</sup> Many small variations in the magnitudes of several rate constants were tested until the best fits between the experiments and the calculations were obtained. Figure 2 shows that by normalizing the observed intensities to  $100\% C_2 H_6$  (14 Torr reactor pressure) both it and 100% C<sub>2</sub>H<sub>6</sub> (7 Torr reactor pressure) runs are well reproduced over the entire reaction period.

In Table I, OH is generated in reactions 1, 6, 8, 12, 15, 20, 24, and 27, and destroyed in reactions 2, 4, 5, 9, 21, and 25. However, in the early stages the major production source of OH is 1, and the major consumption step is 4; H atoms and  $HO_2$  radicals play an important controlling role at later times. During the time interval covered by our measurements, the 29 step model shows that the *steady state* concentration of OH is controlled by several rate processes,

[OH]<sub>ss</sub>

$$\approx \frac{\sum_{i} k_{i}[\mathbf{R}_{i}][\mathbf{O}] + \sum_{j} k_{j}[\mathbf{R}_{j}][\mathbf{H}]}{(k_{4} + k_{5})[\mathbf{O}] + \sum_{r} k_{r}[\mathbf{R}_{r}]}$$
(1)  
$$\approx (k_{4} + k_{5})^{-1} \frac{\sum_{i} k_{i}[\mathbf{R}_{i}] + \sum_{j} k_{j}[\mathbf{R}_{j}]\{[\mathbf{H}]/[\mathbf{O}]\}}{1 + \sum_{r} \{k_{r}/(k_{4} + k_{5})\}\{[\mathbf{R}_{r}]/[\mathbf{O}]\}}$$
(2)

$$\equiv (k_4 + k_5)^{-1} \frac{\alpha + \beta}{1 + \gamma},\tag{3}$$

where

 $\mathbf{R}_i = \mathbf{C}_2\mathbf{H}_6$ , H, HO<sub>2</sub>, CH<sub>3</sub>CHO, HCHO, HCO,  $\mathbf{R}_j = \mathbf{HO}_2$ , O<sub>3</sub>, and  $\mathbf{R}_r = \mathbf{C}_2\mathbf{H}_6$ , H, CH<sub>3</sub>CHO, and HCHO.

Inspection of the computer printouts shows that at 7 Torr operating pressure, 10 ms residence time, 100% C<sub>2</sub>H<sub>6</sub> in He:  $\alpha = 5.57 \text{ s}^{-1}$ ;  $\beta = 1.02 \times 10^{-2} \text{ s}^{-1}$ ;  $\gamma = 8.7 \times 10^{-3}$ . At 14 Torr operating pressure, 10 ms residence time, 100% C<sub>2</sub>H<sub>6</sub>:  $\alpha = 26.6 \text{ s}^{-1}$ ;  $\beta = 0.78 \text{ s}^{-1}$ ;  $\gamma = 3.5 \times 10^{-2}$ .

While these are tightly coupled reactions nonetheless a good estimate of the sensitivity for [OH] production to the various rate constants is obtained from:

$$\frac{\partial \left[\text{OH}\right]_{ss}}{\partial k_i} = \frac{\left[\text{R}_i\right]_i}{k_4 + k_5} \tag{4}$$

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No.	Reactants	Products	<u></u>	k( <i>l</i> /mol s)	Comment
1	C2H6	+ O = C2H5	+ OH	2.00 <i>E</i> 06	(a) 2.71 <i>E</i> 06
2	C2H6	+ OH = C2H5	+ H2O	1.70E08	(a) 1.59E08
3	0	+ O = O2		2.90E05	(a) 2.84 <i>E</i> 05
4	0	+ OH = O2	+ H	2.30E 10	a
5	0	+ OH = HO2		3.74 <i>E</i> 08	b
6	0	+ H = OH		1.18E07	a
7	0	+ O2 = O3		1.52E05	negligible
8	0	+ HO2 = OH	+ O2	3.40 <i>E</i> 10	(c) 3.75 <i>E</i> 10
9	н	+ OH = H2O		1.84 <i>E</i> 08	a {30}
10	н	+H = H2		2.50E06	(a) 2.45E06
11	н	+ O2 = HO2		1.60E07	(d) 7.06E06{31}
12	н	+ HO2 = OH	+ OH	3.89 <i>E</i> 10	а
13	н	+ HO2 $=$ H2O	+0	1.81 <i>E</i> 09	e
14	н	+ HO2 $=$ H2	+ O2	8.00E 09	(e) 3.11 <i>E</i> 09{31}
15	н	+ O3 = O2	+ OH	1.60E 10	e
16	C2H5	+ O = CH3CHO	+ H	5.00E 10	(a) 8.13E 10
17	C2H5	+0 = HCHO	+ CH3	1.00 <i>E</i> 10	(a) 1.62E 10
18	C2H5	+ H = C2H6 (h.p.l	.)	4.00E 10	(a) 3.61 <i>E</i> 10{32}
19	C2H5	+ H = CH3	+ CH3	2.00E 10	(a) 3.60E 10
20	CH3CHO	+0 = CH3CO	+ OH	3.00E08	b
21	CH3CHO	+ OH = CH3CO	+ H2O	1.00E 10	(f) 6.02 <i>E</i> 09
22	CH3CO	+ O = CH3	+ CO2	3.00E 10	b;(a) 9.6E09
23	CH3	+ O = H	+ HCHO	1.00E11	(a) 7.8 <i>E</i> 10{33}
24	нсно	+ OH = HCO	+ OH	1.00E08	a
25	HCHO	+ OH = H2O	+ HCO	5.60E 09	(a) 6.09 <i>E</i> 09
26	нсно	+H = H2	+ HCO	4.00E07	(a) 3.46E07
27	HCO	+0 = OH	+ CO	6.30E 10	(a) 3.0E 10
28	HCO	+ O = H	+ CO2	4.00E 10	(a) 3.0E 10
29	HCO	+H = H2	+ CO	6.60E 10	(g) 8.43 <i>E</i> 10

\* Reference 22 cited indicated value.

<sup>b</sup> Reference 21; we assume  $k_{bi} \propto (1500/T)$  [He].

<sup>c</sup>J. M. Nicovich and P. H. Wine, J. Phys. Chem. 91, 5118 (1987).

<sup>d</sup>K. J. Hsu, J. L. Durant, and F. Kaufman, J. Phys. Chem. 91, 1895 (1987).

<sup>e</sup>D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. Watson, J. Phys. Chem. Ref. Data 13, 1259 (1984).

<sup>f</sup>Estimated from analogous reactions, cited in Ref. 13(a).

<sup>8</sup>R. S. Timonen, E. Ratajczak, and D. Gutman, J. Phys. Chem. 91, 692 (1987).

<sup>h</sup>Specifically, the following reactions were tested as to whether their inclusion affected [OH], and found negligible

	,				
{30}	OH	+ H	= 0	+ H2	(a) 6.32E04
{31}	O2	+ H	= OH		2.1 <i>E</i> -01
<b>{32}</b>	C2H5	+ H	= C2H4	+ H2	(a) 1.81 <i>E</i> 09
{33}	CH3	+ OH	= CH3OH		(a) 3.0E09
					for 5-15 Torr He
{34}	OH	+ OH	= H2O	+0	(a) 1.21E09
{35}	OH	+ HO2	= H2O	+ O2	(a) 4.82 <i>E</i> 10
{36}	OH	+ HCO	= H2O	+ CO	(a) 3.01 <i>E</i> 10
<b>{37}</b>	OH	+ CH3O	= CH2CO	+ H2O	(a) 1.2E 10
			= CH3	+ CO + OH	(a) 3.0E 10
{38}	0	+ CH3O	= CH2O	+ OH	1.0 <i>E</i> 10
			= CH3	+ O2	1.0E 10
{39}	HCO	+ HCO	= H2CO	+ CO	5.0 <i>E</i> 10

These values are listed in Table II at four selected times. The most sensitive rate constant is  $k_1$ , but at later times ( $\approx 15$ ms), the [OH] is also significantly controlled by  $k_6$ . The destruction of [OH] is primarily controlled by  $k_4$ .

$$\frac{\partial \left[\text{OH}\right]_{\text{ss}}}{\partial k_4} = \frac{-\alpha}{\left[k_4 + k_5\right]^2} \tag{5}$$

Besides major consumption of [OH] by reactions (4) and (5), at later times, reactions (9) and (12) assume significant roles.

### THE BORANE OXIDATION

A data set essential for providing the rational for selecting pertinent reactions to be included in kinetic mechanisms for  $B_2H_6 + O(^{3}P)$  is a table of heats of formation and estimated entropies, of all plausible molecular fragments involving B/O/H. The best set, we believe, has been generated by C. F. Melius<sup>24</sup> which we adopted. Then, for a list of 15 B/O/H containing species and 9 O/H species we generated a TABLE II. Sensitivity estimates for  $C_2H_6 + O(^3P)$ .

At 350 K, with $[C_2H_6]_i = 3.22 \ E-06; [O]_i = 2.35 \ E-06; 14 \ Torr total pressure$ $\frac{\partial [OH]_{ss}}{\partial k_i} \approx \frac{[R_i]_i}{k_i + k_i} \left(\frac{\text{mol}\ \ell^{-1}}{\text{mol}^{-1}\ \ell^{s^{-1}}}\right)$								
$k_4 = 2.30 E 10; k_5 = 3$ (Reaction No.) reactant	.74 E 08; time/ms →	1.73	3.47	6.94	13.9	20.8		
(1) C <sub>2</sub> H <sub>6</sub> (6) H (8) HO <sub>2</sub> (20) CH <sub>3</sub> CHO (24) HCHO (27) HCO		1.36 E-16 3.08 E-18 2.81 E-22 5.26 E-19 0.63 E-18 0.61 E-21	$i \rightarrow 1.35$ $i \rightarrow 7.06$ $j \rightarrow 4.71$ $i \rightarrow 6.59$ $i \rightarrow 1.30$ $i \rightarrow 1.26$	1.34 14.7 11.3 6.59 2.07 1.98	1.31 24.5 33.4 5.43 2.38 2.20	1.31 28.1 58.6 4.49 2.25 2.04		

At 350 K, with  $[C_2H_6]_i = 8.3 \text{ E-07}$ ;  $[O]_i = 1.46 \text{ E-06}$ ; 7 Torr total pressure (Reaction No.)

reactant	time/ms→	1.68	5.03	10.10	15.10	
$\overline{(1) C_2 H_6}$		1.36 E-16	5→1.35	1.34	1.31	
(6) H		0.44 <i>E</i> -18	3→1.71	3.95	6.17	
(8) HO <sub>2</sub>		2.81 E-23	4.83	8.94	15.5	
(20) CH <sub>3</sub> CHO		1.03 <i>E</i> -19	)→1.73	1.87	1.82	
(24) HCHO		0.89 <i>E</i> -19	)→3.15	5.49	6.60	
(27) HCO		0.86 <i>E</i> -22	2.→3.06	5.29	6.31	

erated a computer printout of all possible unimolecular and bimolecular reactions (allowing for three molecular products as well) in which these 24 species could participate, subject to the mass conservation constraint. Corresponding  $\Delta H_{300}^{0}$ ,  $\Delta S_{300}^{0}$ , and  $\Delta G_{300}^{0}$  values were calculated for each reaction. The resulting table had over 1000 lines (forward and reverse steps were listed individually). When all reactions with  $\Delta G^{0} > -4.0$  kcal/mol were eliminated, the list shrank to 670; further reductions were achieved by eliminating implausible reactions. A final set of 40 pertinent reactions was identified on the basis of numerous trial kinetic runs.

Anderson and Bauer<sup>4</sup> proposed that the magnitudes of the rate constants for attack on borane adducts by oxygen atoms provide a clue for the initial steps of the oxidation reaction. They also indicated that the mechanism requires the assumption of *two* initiation routes; one in which the O atom abstracts hydrogen(s) from one BH<sub>3</sub> group while ejecting the opposite BH<sub>3</sub>, and the other in which the  $O({}^{3}P)$ directly attacks the boron atom. Fehlner and Strong<sup>25</sup> proposed the initiation step is  $B_2H_6 + O({}^{3}P) \rightarrow H_3B + H_3BO$ . However, abstraction that leads to BH and BH<sub>2</sub> (followed by the formation of OH radicals) is essential for the subsequent production of BO( $A {}^{2}\Pi$ ), which is the source of intense chemiluminescence.

The mechanism that best describes the oxidation of

 $B_2H_6$  by reproducing our [OH] profiles for several concentrations and flow rates is listed in Table III. In the flow tube reactor with  $[B_2H_6]_i = 2.07 \times 10^{-7}$ ,  $[O]_i = 1.11 \times 10^{-6}$ and  $[N_2; He]_i = 3.74 \times 10^{-4} \text{ mol/}\ell$ , at 5 ms after mixing,  $[BH_3]_{calc} = 5.71 \times 10^{-10}; [OH]_{calc} = 3.30 \times 10^{-10}; agree$ ment with the observed value is illustrated in Fig. 3(B). In the lower graph [Fig. 3(C)] note the longer time scales; here  $[B_2H_6]_i = 2.06 \times 10^{-7}$  injected at 14 Torr, 25% diluted in He;  $[O]_i = 1.78 \times 10^{-6}$  with  $[He, N_2]_i = 7.48 \times 10^{-4}$ mol/l. At 6.94 ms,  $[BH_3]_{calc} = 4.84 \times 10^{-10}$ ,  $[OH]_{calc}$ =  $3.28 \times 10^{-10}$ , which checks well with the observed profile. We applied two criteria for an acceptable mechanism: a good match between calculated and recorded shapes of the concentration/time profiles, covering the time range 0.8-35 ms, and quantitative checks of the absolute magnitudes of [OH] over a fourfold concentration range of initial B/H levels. After many, many attempts to select significant reactions and adjust their rate constants, we could not find one set that generates the agreements shown in Figs. 3(A)-3(C)and concurrently accounts for the magnitudes of [OH] recorded when undiluted diborane was injected at 14 Torr {i.e., back pressure corresponds to  $7.5 \times 10^{-4}$  mol/A. Then, observed levels of OH were about one-half of those calculated. We ascribe this discrepancy in part to incomplete mixing.

A sensitivity analysis, parallel to that for  $C_2H_6$  shows that the approximate steady state concentration of OH is

$$[OH]_{ss} \approx (k_{29} + k_{30})^{-1} \frac{\sum_i k_i [R_i] + \sum_j k_j [R_j] \{ [H]/[O] \} + \sum_i k_i [R_i] [O_2]/[O] }{1 + \sum_r \{ k_r / (k_{29} + k_{30}) \} \{ [R_r]/[O] \}}$$
  
=  $(k_{29} + k_{30})^{-1} \frac{\alpha + \beta + \theta}{1 + \gamma}$ ,

(6)

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TABLE III. Mechanism	for B <sub>2</sub> H <sub>6</sub>	$+ O(^{3}P)$	reactions	[350 K]
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No.	Reactants		Products		k(l/mol s)	Comment
1	B <sub>2</sub> H <sub>6</sub>	+ 0	= BH <sub>3</sub>	$+ H_2BOH$	2.00E06	a
2	$B_2H_6$	+0	$= B_2 H_6$	+ OH	9.75 <i>E</i> 06	а
3	$B_2H_6$	+ OH	= H <sub>2</sub> O	$+ B_2H_5$	9.75 <i>E</i> 09	
4	$B_2H_5$	+0	= BH <sub>3</sub>	+ HBOH	3.20E 09	
5	B <sub>2</sub> H <sub>5</sub>	+ H	$= B_2 H_6$		*1.00 <i>E</i> 11°	
6	BO	+ H	= HBO		*9.00E11	x <sup>d</sup>
7	B <sub>2</sub> H <sub>5</sub>	+ OH	$= BH_3$	$+ H_2BOH$	8.00E08	
8	H <sub>2</sub> BOH	+0	⇒ HBOH	+ OH	4.00E 09	
9	H <sub>2</sub> BOH	+0	= OBOH	$+ H_2$	6.50E07	
10	HBOH	+0	= HBO	+ OH	4.50E 09	x
11	BH <sub>3</sub>	+ <b>BH</b> <sub>3</sub>	$= B_2 H_6$		*6.24 <i>E</i> 11	
12	BH,	+0	= HBO	$+H_2$	5.00E07	
13	н	+ HBO	≈ HBOH	-	*1.50E08	
14	BH <sub>3</sub>	+ OH	$= BH_2$	$+ H_2O$	1.00E08	х
15	BH <sub>2</sub>	+ 0	= HBO	+ H	1.00E 09	х
16	HBO	+ 0	$= BO_2$	+ H	1.00E05	
17	HBO	+ OH	≈ BO	$+ H_2O$	7.00E08	
18	HBO	+ OH	$= BO_2$	$+H_{2}$	7.00E08	
19	BH <sub>3</sub>	+0	$= BH_2$	+ OH	5.00E 09	х
20	OBOH	+ 0	$= BO_2$	+ OH	1.00E07	
21	BH,	+0	= BH	+ OH	5.00E07	
22	BH,	+0	= BO	$+ H_2$	5.00E 10	
23	0,	$+ BH_{3}$	= HBOH	+ OH	3.00E06	b
24	<b>O</b> <sub>2</sub>	$+ BH_2$	= HBO	+ OH	1.00E07	
25	0,	+ BH	≔ BO	+ OH	5.00E07	x
26	BÔ	+ OH	= OBOH		*9.50E11	
27	BH	+ OH	$=$ {HBOH}BO	+ H,	1.56E11	
28	0	+0	= 0	-	*4.52E08	
29	он	+ 0	$= 0_{2}$	+ H	2.30E 10	
30	OH	+0	= HO <sub>2</sub>	•	*5.83E11	
31	н	+0	= OH		*1.84E 10	
32	0,	+0	=0		*2.37E08	
33	HO <sub>2</sub>	+0	$= 0_{2}$	+ OH	3.40E 10	
34	н	+ OH	$= H_{2}$		*2.87E11	
35	н	+ H	= H.		*3.90E09	
36	0.	+ H	= HO <sub>2</sub>		*2.50E 10	
37	HO.	+ H	$= OH^2$	+ OH	3.89E 10	
38	HO	+ H	= H <sub>2</sub> O	+0	1.81E09	
39	HO	+ H	= H <sub>2</sub>	$+ \tilde{0}_{2}$	8.00E09	
40	H	+ 0,	= 0.	+ 0H	1.60E 10	
		, 03	<b>U</b> 2	,		

"The overall loss rate in this mechanism is  $3.4 \times$  that reported in Ref. 4.

<sup>b</sup>Consistent with upper limit of rate constant cited by L. Pasternack et al. (NRL Report, 1987).

<sup>c</sup> \*These rate constants (three-body associations) were multiplied by the ambient gas density to convert to bimolecular processes. k 's for 28-40 were transferred from Table I.

<sup>d</sup>x; adjusted from values proposed in Ref. 8. All others were estimated on basis of the magnitudes of their  $\Delta G^0$ 's and adjusted to obtain the indicated [OH] profiles.

where

 $R_i = B_2H_6$ , H, HO<sub>2</sub>, BH<sub>3</sub>, BH<sub>2</sub>, H<sub>2</sub>BOH, HBOH, OBOH,  $R_j = HO_2$ , O<sub>3</sub>; and  $R_l = BH_3$ , BH<sub>2</sub>, BH,  $R_r = B_2H_6$ , H, B<sub>2</sub>H<sub>5</sub>, BH<sub>3</sub>, HBO, BO, BH.

At 7 Torr operating pressure, 8.4 ms residence time, for undiluted  $B_2H_6$ :  $\alpha = 80.8 \text{ s}^{-1}$ ;  $\beta = 1.05 \text{ s}^{-1}$ ;  $\theta = 0.023 \text{ s}^{-1}$ ;  $\gamma = 0.78 \text{ s}^{-1}$ . While one may develop a sensitivity analysis, similar to that for ethane, its significance is of dubious value in view of the many estimated rate constants incorporated in Table III. Inspection of the various magnitudes which contribute to  $\alpha$ ,  $\beta$ ,  $\theta$ , and  $\gamma$  indicates that for [OH] production, reactions (19), (10), and (2) dominate; the destruction of [OH] is controlled primarily by reaction (29), as in the hydrocarbon system. It is interesting to note that whereas the initiating steps 1 and 2 for  $O({}^{3}P)$  with diborane are unique, in general the graphs and the mechanism are analogous to those for  $C_{2}H_{6} + O$ . This should not be surprising, since the dissociation energy of a terminal B/H ( $\approx$  85 kcal/mol) is comparable to that of C/H ( $\approx$  100, 95, and 92 kcal/mol for primary, secondary, and tertiary bonds, respectively).

### CONCLUDING COMMENT

Our experimental OH profiles, along with the model calculations demonstrate that many elementary reactions must be taken into account in order to elucidate the oxidation dynamics of boranes and hydrocarbons. This applies even when the oxidizer/fuel ratio is relatively large. For ethane it is unlikely that small changes in the proposed rate



FIG. 3. [OH] observed (O and O) and calculated via the mechanism listed in Table III (350 K).

constants will alter the shapes of the OH profiles. We reiterate that in developing the mechanism presented in Table III, about 380 reactions were considered; approximately 100 were tested in various combinations, and more than half were found not to influence the levels of OH, assuming reasonable magnitudes for the corresponding rate constants. We have no basis, at this time, for estimating the relative importance of reactions such as

$$B_{3}H_{7} + O \rightarrow B_{3}H_{6} + OH$$
$$B_{2}H_{5} + BH.$$

While at this stage we can select the major contributing processes that generate OH, clearly these are closely coupled to other concurrent reactions. For diborane much remains to be measured, to confirm the proposed mechanism. Monitoring species other than OH is essential. One should focus on the dominant species, listed in descending concentration levels: HBO ( $\sim 10^{-7}$  M), BO( $10^{-7}$ ), BH( $10^{-8}$ ), HBOH( $7 \times 10^{-9}$ ), BO( $10^{-9}$ ), BH<sub>2</sub>( $10^{-9}$ ), and OBOH( $4 \times 10^{-10}$  M). These are predicted by the proposed mechanism for undiluted B<sub>2</sub>H<sub>6</sub> injected into an excess of [O] at 7 Torr, total pressure.

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