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<p>To aid in the development of boron-enhanced fluoronitramino explosives, the kinetics of individual reactions are measured over wide temperature ranges. The following rate expressions, in <math>\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}</math>, were obtained. For <math>\text{BO}_2 + \text{H}_2 \rightarrow \text{HOBO} + \text{H}</math> <math>k(500-1250 \text{ K}) = 3.6 \times 10^{-11} \exp(-4198 \text{ K/T})</math>, for <math>\text{BO} + \text{CO}_2 \rightarrow \text{BO}_2 + \text{CO}</math> <math>k(780-1200 \text{ K}) &lt; 2.7 \times 10^{-14}</math>, for <math>\text{BO}_2 + \text{CO} \rightarrow \text{BO} + \text{CO}_2</math> <math>k(1000 \text{ K}) &lt; 6.0 \times 10^{-14}</math>, for <math>\text{BO} + \text{O}_2 \rightarrow \text{BO}_2 + \text{O}</math> <math>k(300-960 \text{ K}) = 7.9 \times 10^{-12} \exp(161 \text{ K/T})</math>.</p>						
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## PROGRESS

### Introduction

Our goals are:

- (1) to make accurate measurements, over wide temperature ranges, of rate coefficients for boron combustion in C/H/N/O/F environments, of importance to the development of new underwater explosives, and
- (2) to use the measurements to obtain a further understanding, to allow predictions for additional reactions occurring with such explosives.

Reactions for study are selected on the basis of modeling studies.<sup>1-4</sup> The results, in turn, allow improvement of the models. In the past year measurements have been made on



A High-Temperature Fast-Flow Reactor (HTFFR) was used to measure rate coefficients for reaction 1 and upper limits for 2a and 2b. The High-Temperature Photochemistry (HTP) technique was used to obtain an upper limit for 2a, as well as to measure rate coefficients for reaction 3.

### Experimental

The HTFFR and HTP reactors and procedures have been described frequently.<sup>5</sup> The reactions were studied in Ar bath gas under pseudo first-order conditions with BO or BO<sub>2</sub> as the minor reactant. For BO production in the HTFFR studies, a mixture of B and N atoms was produced by passing a trace of diborane, B<sub>2</sub>H<sub>6</sub>, mixed with N<sub>2</sub> in Ar bath gas through a microwave discharge. NO was added downstream to produce O atoms, via N + NO → N<sub>2</sub> + O, which resulted in BO formation, Fig. 1. BO<sub>2</sub> was produced by reacting BCl<sub>3</sub> with the products resulting from passing a CO<sub>2</sub>/Ar mixture through a microwave discharge, Fig. 2. For the HTP studies, BO radicals were produced by multi-photon dissociation of BCl<sub>2</sub>(OCH<sub>3</sub>).<sup>6</sup>

The relative [BO] was monitored via laser-induced fluorescence of the A<sup>2</sup>Π-X<sup>2</sup>Σ (1,1) transition at 436 nm, pumped at 403.55 nm on the (1,0) transition.<sup>7</sup> Relative [BO<sub>2</sub>] was monitored by pumping the B<sup>2</sup>Σ-X<sup>2</sup>Π (000-000) transition at 406.7 nm and observing the A<sup>2</sup>Π-X<sup>2</sup>Π (002-000) transition at 435.8 nm.<sup>8</sup>

### Results

#### BO<sub>2</sub> + H<sub>2</sub>

Rate coefficient measurements were made from 500 - 1250 K, at total pressures from 4.1 - 9.3 mbar, corresponding to total concentrations of 3.0 x 10<sup>16</sup> to 6.7 x 10<sup>16</sup>.

molecules  $\text{cm}^{-3}$ , average gas velocities from 21 to 106  $\text{m s}^{-1}$ , and reaction zone lengths selected at 10 or 20 cm. The data were fitted to a  $k(T) = A \exp(-E/T)$  expression, by weighted linear regression,<sup>9</sup> to yield

$$k_1(500-1250 \text{ K}) = 3.6 \times 10^{-11} \exp(-4198 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

This result is compared in Fig. 3 to the expression  $k_1(T) = 3.0 \times 10^{-12} \exp(-1475 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  estimated by Brown *et. al.*,<sup>1-3</sup> which may be seen to differ significantly. The primary temperature range of interest for boron combustion is 1800 - 3000 K.<sup>1-4</sup> Extrapolation of eq. 4 to these temperatures would result in rate coefficients approximately 3 - 5 times greater than used in these models.

### BO + CO<sub>2</sub>

This reaction was studied between 780 to 1200 K in an HTFFR, and yielded the upper limit

$$k_{2a}(780 - 1200 \text{ K}) < 2.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

Measurements by the HTP technique mirrored this result:

$$k_{2a}(300 - 870 \text{ K}) < 9.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

The Brown *et. al.* model uses  $k_{2a} = 1.8 \times 10^{-11} T^{0.37} \exp(-7900 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which at 1200 K is more than an order of magnitude larger than the upper limit of eq. 6 and would indicate a fast reaction in the 1800 - 3000 K range.

The reverse reaction, 2b, was studied at 1000 K and gave an upper limit

$$k_{2b}(1000 \text{ K}) < 6.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

Based on the Gibbs free energy of reaction 2a,  $-14.6 \text{ kJ mol}^{-1}$  at 1000 K, and its experimental upper limit (eq. 5), the upper limit at 1000 K for reaction 2b is calculated to be  $4.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , consistent with eq. 7. To help understand why reactions 2a and b are so slow we plan to make *ab initio* calculations to find transition states and associated activation barriers.

### BO + O<sub>2</sub>

This reaction was studied over the 300 to 960 K temperature range at pressures from 67 to 271 mbar ( $9.7 \times 10^{17}$  to  $6.5 \times 10^{18}$  molecules  $\text{cm}^{-3}$ ). At temperatures of 300, 500, and 950 K the reaction was found to be pressure independent. The results may be seen to be in agreement with the study by Stanton *et. al.*,<sup>6</sup> Fig. 4; those authors had limited the pressure dependence study to room temperature. The combined data sets were fitted as above to yield

$$k_3(300 - 960 \text{ K}) = 7.9 \times 10^{-12} \exp(161 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (8)$$



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Gentlemen:

Enclosed please find the contractually required 2 copies of the annual report on the referenced grant.

Sincerely,

Arthur Fontijn  
Professor & Head of the Department

AF:jm  
Enc.

## PLANS

Reactions to be studied will be selected on the basis of the ongoing Aerodyne-Princeton modeling work.<sup>1-3</sup> These include the reactions of BO with N<sub>2</sub>O, HCl, and HF, and of BF with BF<sub>3</sub>, O<sub>2</sub>, and H<sub>2</sub>O.

As already mentioned, we plan ab initio studies in an attempt to explain the low reactivity of reaction (2).

In last year's progress report, we reported on the BO + HCl reaction. There are three exothermic spin-allowed exit channels for this reaction: HBO + Cl<sub>2</sub>, OBCl + H, and BCl + OH. By making use of an HTFFR mass-spectrometer facility, developed recently with other support,<sup>10</sup> we plan to try to distinguish between these.

## PARTICIPANTS AND CONTACTS

G.T. Dalakos was fully supported by this grant. For the HTP work he received assistance from J-D.R. Rocha, for the HTFFR he worked with D.P. Belyung, who is supported by an AFOSR-AASERT grant and Q. Zhang, who is supported by NSF. We thank Dr. R.A. Yetter for several informative discussions.

## PUBLICATIONS AND AWARDS

1. D.P. Belyung, G.T. Dalakos, Q. Zhang, J-D.R. Rocha, and A. Fontijn, "Wide-Temperature Range Studies of BO and BO<sub>2</sub> Reactions", Extended Abstract for presentation at the Eastern States Section of the Combustion Institute meeting, December 9-11, 1996.
2. G.T. Dalakos, "BO Reactions Over A Wide Temperature Range", M.Sc. Thesis, Rensselaer Polytechnic Institute, Troy, NY, May 1996.

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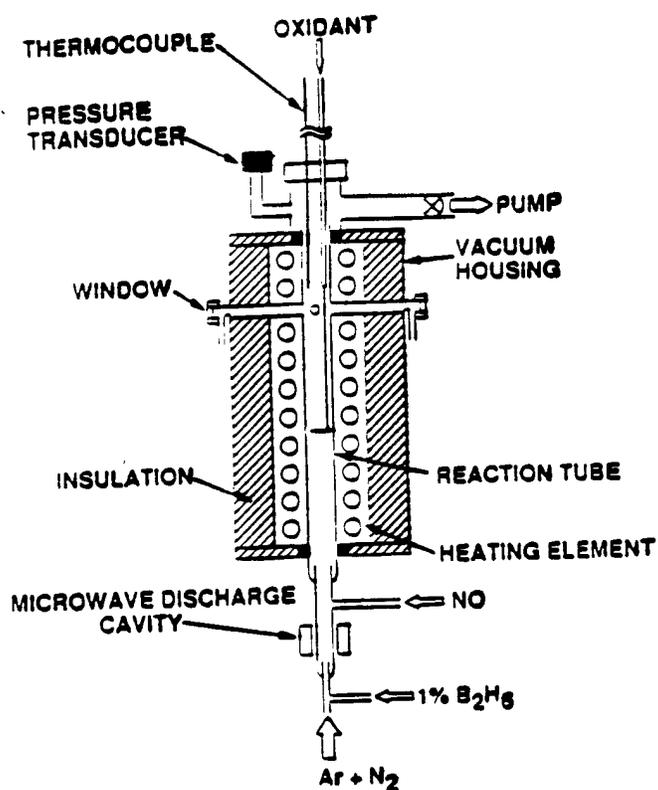


Figure 1. Schematic of the HTFFR BO production method

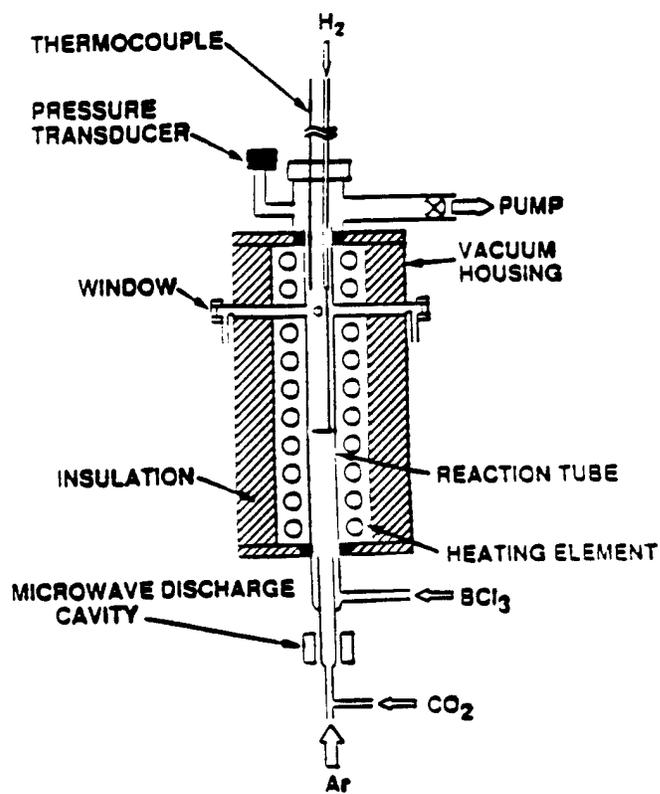


Figure 2. Schematic of the HTFFR BO<sub>2</sub> production method

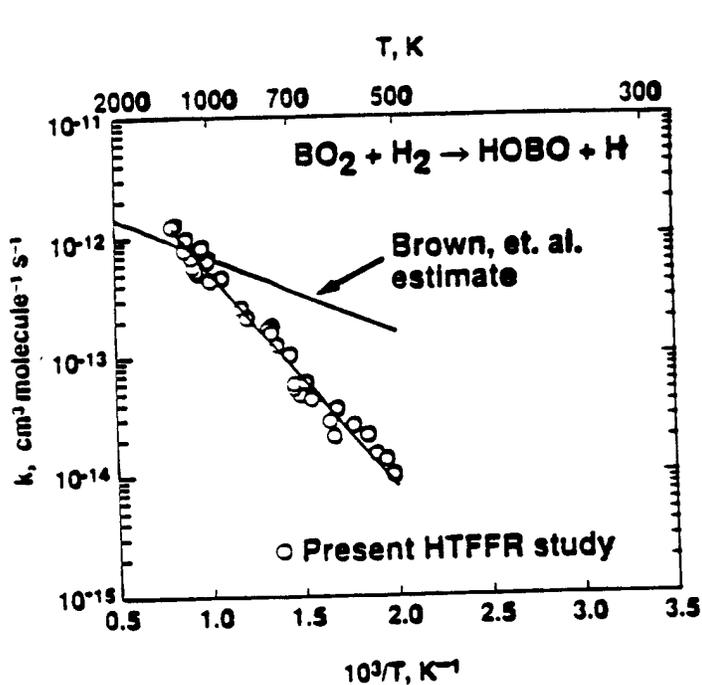


Figure 3. Summary of the BO<sub>2</sub> + H<sub>2</sub> rate coefficients

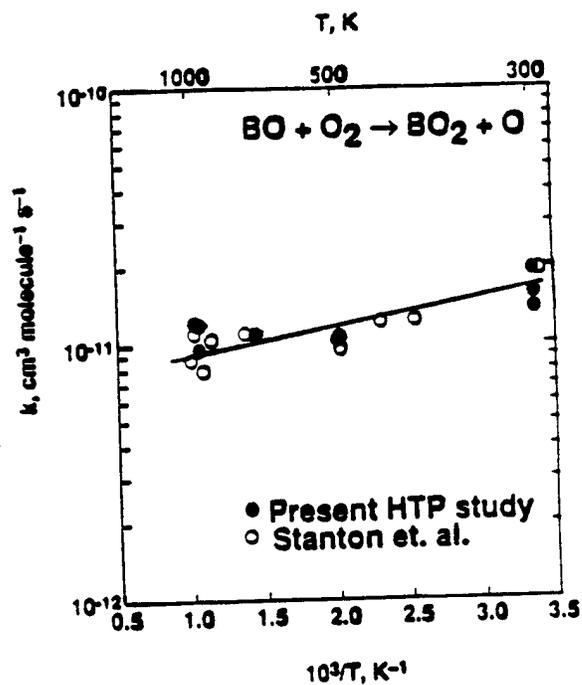


Figure 4. Summary of the BO + O<sub>2</sub> rate coefficients