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Form Approved  
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE <p style="text-align: center;">January 1998</p>	3. REPORT TYPE AND DATES COVERED <p style="text-align: center;">Final 10/15/93 - 11/14/97</p>
4. TITLE AND SUBTITLE <p style="text-align: center;">Gas-Phase Kinetics Measurements for Underwater Explosives</p>		5. FUNDING NUMBERS G: N-00014-94-1-0097 PE: 601153N PR: 02402 TA: 010
6. AUTHOR(S) <p style="text-align: center;">Arthur Fontijn</p>		8. PERFORMING ORGANIZATION REPORT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Rensselaer Polytechnic Institute Department of Chemical Engineering Troy, NY 12180-3590		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) ONR, Code 333 800 North Quincy St., Room 504 Arlington, VA 22217		10. SPONSORING / MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES		19980130 068
a. DISTRIBUTION / AVAILABILITY STATEMENT <p style="text-align: center;">Unlimited</p>		Unclassified/Unlimited
13. ABSTRACT (Maximum 200 words)  To aid in the development of boron-enhanced fluoronitramino explosives, the kinetics of individual reactions have been measured over wide temperature ranges. Results obtained are, for $BO + O_2 \rightarrow BO_2 + O$ (1) $k(298 - 960 K) = 7.9 \times 10^{-12} \exp(161 K/T)$ and for $BO + HCl \rightarrow$ products (2) $k(293 - 760 K) = 6.3 \times 10^{-13} \exp(-1403 K/T)$ , both in units of $cm^3 \text{ molecule}^{-1} s^{-1}$ . Upper limits are found for $BO + CO_2 \rightarrow BO_2 + CO$ (3). Reactions (1) and (2) have pre-exponentials two orders of magnitude smaller than the corresponding AIO reactions. Evidence is presented suggesting that all six reactions proceed through intermediate complexes, which for BO are thought to readily dissociate back to the reactants. This would explain why reaction (3) is too slow for observation. That reaction, and its reverse, were considered as very sensitive in models for B/O/H/C system combustion.  <p style="text-align: right;">DTIC QUALITY INSPECTED 2</p>		
14. SUBJECT TERMS Explosives Fluoro-Nitramino Boron		15. NUMBER OF PAGES <p style="text-align: center;">27</p>
17. SECURITY CLASSIFICATION OF REPORT Unclassified		16. PRICE CODE
18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT <p style="text-align: center;">UL</p>

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## Introduction

The high gravimetric heating value of boron has led to a recurrent interest in its use in explosives and rocket propellants. Particularly ONR developments in fluoronitramino-based explosives have rekindled interest in boron combustion behavior. A group at Aerodyne and Princeton has developed kinetic models for boron combustion in various environments and have estimated rate coefficients.<sup>1-3</sup> However, measured data are lacking for nearly all key reactions. Guided by these models, we have measured some of these reactions in our unique high temperature reactors of the HTFFR (high-temperature fast-flow reactor) and HTP (high-temperature photochemistry) type. These allow elementary combustion reactions to be studied in isolation.

The goals of this program were:

- (i) to make accurate measurements, over wide temperature ranges, of rate coefficients for boron combustion, needed for models used in the development of new underwater explosives, and
- (ii) to use the measurements to obtain a further understanding, to allow predictions for additional reactions occurring with such explosives.

## Achievements

The experimental techniques used, the major results and their interpretation are contained in a publication prepared upon completion of the work. It is given as Appendix A of this report.

Results from this work also appear in a number of theses. In the first place:

George T. Dalakos, "BO Reactions over a Wide Temperature Range", MS thesis, Rensselaer Polytechnic Institute, Troy, NY, May 1996,

also in:

David P. Belyung, "Kinetics of Metal Combustion Reactions", Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, NY, March 1997.

A further MS thesis by Mr. Qifeng Zhang is in preparation.

## Participants and Contacts

In addition to Dr. Belyung, Mr. Dalakos and Mr. Zhang, William F. Flaherty and John-David R. Rocha have worked on this grant. We have had several useful discussions with Dr. R.A. Yetter on the Aerodyne-Princeton models.

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*Submitted to the 27<sup>th</sup> Symposium (International) on Combustion*

## Wide-Temperature Range Kinetics of the BO Reactions with O<sub>2</sub>, HCl, and CO<sub>2</sub>. Comparison to AlO Reactions.

David P. Belyung, George T. Dalakos, John-David R. Rocha, and Arthur Fontijn  
*High-Temperature Reaction Kinetics Laboratory  
The Isermann Department of Chemical Engineering  
Rensselaer Polytechnic Institute  
Troy, NY 12180-3590*

### **Corresponding Author:**

Arthur Fontijn  
High-Temperature Reaction Kinetics Laboratory  
The Isermann Department of Chemical Engineering  
Rensselaer Polytechnic Institute  
110 8<sup>th</sup> Street  
Troy, NY, USA 12180  
PH: (518) 276-6508  
FAX: (518) 276-4030  
E-MAIL: fontia@rpi.edu

### **Word Count:**

TEXT (by computer) =	2532
FIGURES/TABLES @ 200 × 7 =	1400
EQUATIONS @ 21 × 21 =	<u>441</u>
TOTAL =	4373

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David P. Belyung, George T. Dalakos, John-David R. Rocha and Arthur Fontijn

*High-Temperature Reaction Kinetics Laboratory, The Isermann Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180-3590*

**Abstract**

Rate coefficients for the title BO reactions have been measured by using laser-induced fluorescence in high-temperature reactors. The results obtained are, for  $\text{BO} + \text{O}_2 \rightarrow \text{BO}_2 + \text{O}$  (1)  $k(298 - 960 \text{ K}) = 7.9 \times 10^{-12} \exp(161 \text{ K}/T)$  and for  $\text{BO} + \text{HCl} \rightarrow \text{products}$  (2)  $k(293 - 760 \text{ K}) = 6.3 \times 10^{-13} \exp(-1403 \text{ K}/T)$ , both in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Upper limits are found for  $\text{BO} + \text{CO}_2 \rightarrow \text{BO}_2 + \text{CO}$  (3). Reactions (1) and (2) have pre-exponentials two orders of magnitude smaller than the corresponding AIO reactions. Evidence is presented suggesting that all six reactions proceed through intermediate complexes, which for BO are thought to readily dissociate back to the reactants. This would explain why reaction (3) is too slow for observation. That reaction, and its reverse, were considered as very sensitive in models for B/O/H/C system combustion.

## Introduction

The high gravimetric heat of combustion value of boron has led to a recurrent interest in its use in explosives and rocket propellants [1]. A group of investigators at Aerodyne and Princeton have developed models for boron combustion, first for homogeneous reactions in B/O/H/C systems [2-4], later for fluorine containing systems [5] and heterogeneous processes [6], as well. Pasternak also has reported on a B/O/H/C model [7]. In those studies  $k(T)$  expressions have been estimated and key reactions have been identified. Only two of these key reactions have been previously measured [8-9]. The present work extends the measured data base. Results are reported for



Of these, only reaction (1) has been studied before, over somewhat more limited conditions [8]. Reaction (2) was included to obtain an idea of the effect of a halogen in the system prior to investigations with fluorine species in future experimental work. The results of these BO reactions are compared to those of our earlier studies of AlO reactions.

## Technique

An HTFFR (high-temperature fast-flow reactor) and an HTP (high-temperature photochemistry) reactor have been used in this work. The reaction with  $\text{O}_2$  was first attempted in an HTFFR, but because of severe scatter an HTP reactor was used instead. The HCl reaction was

studied in an HTFFR, and both reactor types were employed for the investigation of the CO<sub>2</sub> reaction.

### *HTP Measurements*

The newer type HTP reactor (B), discussed by Mahmud et al. [10], was used. The general experimental arrangements, operational procedures, and data reduction techniques for this real time pseudo-static technique have been described [11-12] and summarized [13]. This reactor includes a 5-cm diameter alumina reaction tube surrounded in sequence by 20 alternatively stacked SiC heating rods, insulation, and a water-cooled steel vacuum chamber. BO radicals were produced via 193 nm multi-photon dissociation of dichloromethyl borate, BCl<sub>2</sub>(OCH<sub>3</sub>), which together with the O<sub>2</sub> or CO<sub>2</sub> flowed in through a cooled inlet. The BCl<sub>2</sub>(OCH<sub>3</sub>) was synthesized as described by Gerrard and Lappert [14]. The relative [BO] was monitored by laser-induced fluorescence, LIF, of the A<sup>2</sup>Π-X<sup>2</sup>Σ(1,1) transition at 436.3 nm, pumped at 403.55 nm on the (1,0) transition [15]. A light filter (λ<sub>0</sub> = 435.8 nm; fwhm = 8.5 nm) was placed in front of the photomultiplier tube to reduce scattered light and background radiation.

The reactions were studied under pseudo-first order conditions with [BO] << [X] << [Ar], where X = (O<sub>2</sub> or CO<sub>2</sub>). The fluorescence intensity *I*, proportional to [BO], can be described by

$$I = I_0 \exp(-k_{\text{ps1}} t) + B \quad (4)$$

where *I*<sub>0</sub> is the intensity at time *t* = 0, *k*<sub>ps1</sub> is the pseudo-first order rate coefficient and *B* is the background intensity, which is mostly due to scattered light. The values of *k*<sub>ps1</sub>(±σ<sub>kps1</sub>) were obtained using a nonlinear least-squares fitting routine [16], of the observed *I* vs. *t* decay plots, to equation 4. In addition, a two-stage residual analysis [?] was used to verify the exponentiality of each decay. Usually five to eight values of *k*<sub>ps1</sub> vs. [X], from 0 to [X]<sub>max</sub>, were acquired at each set

of conditions. Bimolecular rate coefficients,  $k_i$ , and their statistical precision,  $\sigma_{k_i}$ , were derived from the slopes of weighted linear plots of  $k_{psl}$  vs.  $[X]$  [17].

The gases used were Ar, from the liquid (Praxair 99.998%), O<sub>2</sub> (Matheson 99.95%), and "Bone Dry" CO<sub>2</sub> (Matheson 99.5%). Trimethyl borate (B(OCH<sub>3</sub>)<sub>3</sub>, Aldrich 99%) and BCl<sub>3</sub> (Matheson 99.9%) were used in the synthesis of BCl<sub>2</sub>(OCH<sub>3</sub>).

#### *HTFFR Measurements*

The HTFFR technique and the data analysis procedures have been discussed several times [13,18-19]. Briefly, a vertical industrial grade quartz or mullite reaction tube is radiatively heated by two horizontal columns of resistively heated SiC rods inside an insulated, water-cooled vacuum housing (60 cm long, 2.2 cm i.d.). The BO is produced on the upstream side, and is entrained by the bath gas Ar. The second reactant is introduced through a movable quartz nozzle, 10 or 20 cm upstream from the observation window where the relative [BO] is measured by LIF.

BO was produced by adding a microwave discharge flow tube upstream from the HTFFR, cf. Fig. 1. Two methods were developed for BO production. By the first, about 1 ppm B<sub>2</sub>H<sub>6</sub>, together with 2000 ppm N<sub>2</sub> in Ar, is discharged to produce B atoms and active nitrogen. NO is then added to generate O atoms, which lead to BO via the B + O + M reaction. Alternatively, a discharged mixture of 2 ppm B<sub>2</sub>H<sub>6</sub> in Ar was mixed with SO<sub>2</sub>, which rapidly [20] oxidizes B to BO. Relative BO concentrations were monitored in the same manner as described for the HTP experiments. Ar and CO<sub>2</sub> were obtained as given above. The other gases, i.e. HCl Semiconductor 4.5 purity grade, B<sub>2</sub>H<sub>6</sub> Semiconductor grade 5.0, 1.0% in Ar, and SO<sub>2</sub> anhydrous 99.8%, 1.07% in Ar, were all obtained from Matheson.

Measurements were again made under pseudo-first order conditions in the stationary inlet

mode [18], yielding  $k_{ps1} \pm \sigma_{kps1}$ . Rate coefficients,  $k_i$ , for each temperature, pressure, and average velocity were obtained by using five different oxidant concentrations providing a variation by a factor of 5.  $k_i$  and  $\sigma_{k_i}$  were calculated by applying a weighted linear regression [17] to plots of  $\ln [\text{BO}]_{\text{relative}}$  (corresponding to integrated fluorescence intensities) vs. [second reactant]. These calculations yielded straight lines with slopes equal to  $-k_i t \pm \sigma_{k_i}$ , where  $t$  is reaction time.

## Results and Discussion

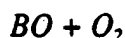


Table 1 lists the measurements of reaction (1) over the 298 to 960 K temperature range. Results above 960 K were irreproducible due to breakdown of the BO precursor. The rate coefficients,  $k_i$ , are well fitted by a simple Arrhenius expression,  $k(T) = A \exp(-E / RT)$ , using a weighted linear regression [21], to yield

$$k_1(298 - 960 \text{ K}) = 9.8 \times 10^{-12} \exp(55 \text{ K} / T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

with variances and covariance [22-23] of  $\sigma_A^2 = 1.38 \times 10^{-2} \text{ A}^2$ ,  $\sigma_E^2 = 3.36 \times 10^3$ , and  $\sigma_{AE} = 6.54 \text{ A}$ . Using  $2\sigma$  statistical bounds gives precision levels of  $\pm 13$  to  $\pm 19\%$  depending on temperature. Allowing  $\pm 20\%$  for possible systematic errors leads to confidence limits from  $\pm 26$  to  $\pm 29\%$ . Plots of the residuals  $(k_i - k_{fit}) / k_{fit}$  show the rate coefficients to be independent of the average gas velocity,  $\bar{v}$ , the inlet to reaction zone length,  $z$ , the total gas concentration,  $[\text{M}]$ , and the corresponding pressures.

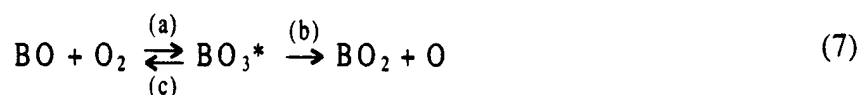
There is good agreement between the present measurements and those of Stanton et al [8]. Both data sets are shown in Figure 2, combined these yield

$$k_1(298 - 960 \text{ K}) = 7.9 \times 10^{-12} \exp(161 \text{ K} / T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

and relevant statistics of  $\sigma_A^2 = 4.70 \times 10^{-3} \text{ A}^2$ ,  $\sigma_E^2 = 1.18 \times 10^3$ , and  $\sigma_{AE} = 2.20 \text{ A}$ . Depending on

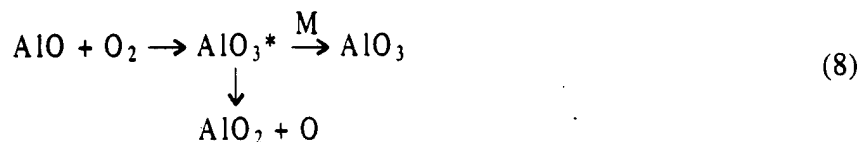
temperature, precision levels are  $\pm 9$  to  $\pm 16\%$ , with corresponding confidence limits of  $\pm 24$  to  $\pm 27\%$ , all at  $2\sigma$  statistical levels.

Reaction (1) is exothermic by  $36 \pm 6 \text{ kJ mol}^{-1}$  [24]. Stanton et al. had established the pressure independence at room temperature only [8]. The present work has confirmed this for the temperature range covered. This is important as it confirms that their mechanism [8], which also takes into account the negative temperature dependence,



is valid for this range and presumably higher temperatures. Implicit in this scheme is that  $k_c > k_b$ . Based on an SCF/CI calculation they [8] proposed a structure for the intermediate consisting of a cyclic  $\text{BO}_2$  portion with the third O attached directly to the B atom. The small pre-exponential of eq. 6 suggests an intermediate complex that preferentially dissociates back to the reactants with no net reaction.

The reaction between  $\text{AlO}$  and  $\text{O}_2$  is also thought to proceed via an intermediate complex, probably of similar structure as that of  $\text{BO}_3$  [25]. This reaction is of third order below 1000 K in the 7 to 100 mbar pressure range, suggesting stabilization of  $\text{AlO}_3$ . At higher temperatures a second order process could be measured,  $k(1200 - 1690 \text{ K}) = 7.7 \times 10^{-10} \exp(-10008 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The most probable reaction mechanism here is [25]



The large pre-exponential suggests little or no dissociation of  $\text{AlO}_3$  back to the reactants. The third order behavior also indicates a more stable  $\text{AlO}_3$  intermediate than the  $\text{BO}_3$  intermediate. The  $\text{AlO}_2 + \text{O}$  formation is endothermic by  $96 \pm 40 \text{ kJ mol}^{-1}$ .

### *BO + HCl*

Reaction 2 was studied in an HTFFR from 290 to 760 K. The reaction conditions and rate coefficients are listed in Table 2. Analysis of the residuals shows that the data are independent of total concentration, pressure, average gas velocity, and reaction zone length. The data (Figure 3) are well fitted by an Arrhenius expression. The regression analysis [21] yields

$$k_2(290 - 760 \text{ K}) = 6.3 \times 10^{-13} \exp(-1403 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (9)$$

with variances and covariance of  $\sigma_A^2 = 8.12 \times 10^{-2} \text{ A}^2$ ,  $\sigma_E^2 = 1.86 \times 10^4$ , and  $\sigma_{AE} = 37.8 \text{ A}$ . The calculated precision levels range from  $\pm 25$  to  $\pm 38\%$  at the  $2\sigma$  statistical level, depending on temperature. Allowing for  $\pm 20\%$  for possible systematic errors and  $\pm 10\%$  in the flow profile factor [18] the corresponding confidence levels vary from  $\pm 34$  to  $\pm 44\%$ .

This result may be compared to that of the  $\text{AlO} + \text{HCl}$  reaction [26], for which also no pressure dependence was observed, and  $k(440 - 1590 \text{ K}) = 5.6 \times 10^{-11} \exp(-139 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Again the  $\text{BO}$  reaction has a two order of magnitude lower pre-exponential. It is tempting to attribute this to the reactions proceeding through an intermediate complex, which is less stable in the  $\text{BO}$  case. There is considerable evidence from matrix studies that B atoms can insert into covalent bonds [27]. There are previous indications that  $\text{AlO}$  can insert in covalent bonds [28] and that free radical metallic species can insert in  $\text{HCl}$  [29-30]. However, the most compelling indication for the existence of such complexes comes from the *ab initio* studies of

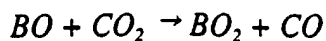
Soto on the BO + HF reaction. These indicate that this reaction proceeds through an  $\overset{\text{O}}{\text{FBH}}$  complex [31] and an FBOH complex [31-32], both dissociating to FBO + H. The equivalent processes here would thus be:



Other dissociation channels can not *a priori* be excluded. Thus



could be involved. The reaction leading to HAlO would be  $180 \pm 92 \text{ kJ mol}^{-1}$  endothermic and can be excluded on that ground. Products containing the weak ClO bond can probably similarly be disregarded. The  $\Delta H$  value for HBO used here is that of Page [33] and those for ClBO and ClAlO are from Chen, Hase, and Schlegel [34], who show the JANAF data for these compounds to be in need of correction. The mechanism for the AlO + HCl reaction differs from our original proposal [26], where direct abstraction was assumed to lead to ClAlO and/or AlOH. Based on current methods, positive identification of the products for reactions (10) and (11) can not be made. An *ab initio* study would be most useful to help remove the current mechanistic uncertainties.



This reaction, for which  $\Delta H_{298}^\circ = -2 \pm 16 \text{ kJ mol}^{-1}$ , was studied over the 298 - 870 K temperature range by the HTP technique and from 780 - 1200 K in an HTFFR. In neither reactor could any reaction be observed. Upper limits to the rate coefficients were obtained [35] by taking  $2\sigma_{\text{kpsi}}$ , as defined in the Technique section, and dividing it by the  $[CO_2]_{\text{max}}$  for the HTP experiments, or  $[CO_2]_{\text{max}} - [CO_2]_{\text{min}} = 0.8[CO_2]_{\text{max}}$  for the HTFFR experiments. The results are given in Tables 3 and 4. An HTFFR study of the reverse process [36]



also showed no reaction, in accord with the present data.

This apparent lack of reaction was somewhat unexpected in view of the key role reactions (3) and (-3) were estimated to have in the B/O/H/C models [2-4]. However, an ongoing *ab initio* study [37] of these reactions has found no direct pathway connecting the reactants and products, suggesting that here too a bound intermediate may be involved. Work on Al supports this idea. Thus, chemiluminescence observations on the  $Al + CO_2 + O_3$  reaction system have given evidence for the formation of an  $OAlCO_2$  complex [38]. Room temperature measurements on the  $AlO + CO_2$  reaction [39] found the reaction to be pressure dependent, indicating the formation of such a complex. An early HTFFR study from 500 to 1300 K yielded rate coefficients in the  $1 \times 10^{-13}$  to  $1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  range, with wide scatter in the results [40]. Subsequent work with a much improved HTFFR on the  $AlO + O_2$  reaction [25] has shown that a pressure-dependence may be hidden within such scatter, i.e. that a complex can form at these temperatures as well.

It thus appears probable that the reason for the apparent lack of reaction is that the

mechanism is similar to that of the other BO reactions reported here, i.e. has a small pre-exponential due to formation of an intermediate complex readily dissociating back to the reactants. For the CO<sub>2</sub> reaction this then results in rate coefficients too low for measurement by the present techniques. The Al analogy would suggest an OBCO<sub>2</sub> structure for this intermediate. Matrix [27,41-42] and *ab initio* [43] studies have shown the existence of such OBC structures.

### Conclusions

Three reactions of BO have been studied and compared to their AlO equivalents. The O<sub>2</sub> and HCl reactions show much smaller pre-exponentials in their  $k(T)$  expressions than the corresponding AlO reactions. No reaction with CO<sub>2</sub> could be observed, contrary to the AlO analog. It is suggested that all these reactions proceed through intermediate complexes, which for BO have a high probability for dissociation to the reactants. The evidence presented suggests, for the O<sub>2</sub> and CO<sub>2</sub> reactions, that in these complexes the B is bonded to the reaction partner and the O remains bonded to the B only. For the nature of such BO bonds in complexes Lanzisera and Andrews [41] have indicated partially dative bonds in which an oxygen lone pair bonds with the empty boron p-orbital. For the HCl reaction,  $\begin{array}{c} \text{O} \\ | \\ \text{C} \text{B} \text{H} \end{array}$  is similarly a likely structure for the intermediate, but the ClBOH configuration may also play a role.

## **Acknowledgements**

We thank Dr. P. Marshall for helpful discussions, Dr. R. A. Yetter for information on the boron models, and W. F. Flaherty for his technical assistance. This work was supported by the Office of Naval Research (Grant N00014-94-1-0097), Dr. R.S. Miller, Program Officer, and the Air Force Office of Scientific Research (Grant F49620-95-1-0473), Dr. M.A. Birkan, Program Manager.

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Table 1. Summary of HTP Rate Coefficient Measurements on BO + O<sub>2</sub>

$T^a$ (K)	$P$ (mbar)	$[M]$ ( $10^{18} \text{ cm}^{-3}$ )	$[\text{O}_2]_{\text{max}}$ ( $10^{15} \text{ cm}^{-3}$ )	$F$ (mJ)	$\bar{v}$ ( $\text{cm s}^{-1}$ )	$z$ (cm)	$k_i \pm \sigma_{k_i}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
298	73	1.8	2.3	20	22.3	14	$1.53 \pm 0.19$ (-11) <sup>b</sup>
298	133	3.2	13.0	20	10.6	14	$1.94 \pm 0.72$ (-11)
298	266	6.5	1.9	20	6.04	14	$1.36 \pm 0.19$ (-11)
488	149	2.2	5.9	20	19.7	14	$1.01 \pm 0.05$ (-11)
488	201	3.0	6.1	20	13.3	14	$0.96 \pm 0.16$ (-11)
499	67	1.0	2.3	20	35.3	7.5	$1.05 \pm 0.10$ (-11)
692	166	1.8	2.8	20	20.7	10	$1.09 \pm 0.14$ (-11)
952	271	2.1	4.1	20	17.1	5	$1.26 \pm 0.28$ (-11)
955	229	1.7	3.9	20	20.2	5	$0.97 \pm 0.16$ (-11)
960	128	1.0	2.4	20	36.9	5	$1.28 \pm 0.10$ (-11)

a)  $\sigma_T / T = \pm 2\%$ .

b) Should be read as  $(1.53 \pm 0.19) \times 10^{-11}$ .

**Table 2. Summary of HTFFR Rate Coefficient Measurements on BO + HCl**

$T^a$ (K)	$P$ (mbar)	[M] ( $10^{17} \text{ cm}^{-3}$ )	[HCl] $_{\text{max}}$ ( $10^{15} \text{ cm}^{-3}$ )	$F$	$\bar{v}$ ( $\text{m s}^{-1}$ )	$z$ (cm)	$k_i \pm \sigma_{k_i}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
293	13.9	3.4	32.1	871	17	10	$8.34 \pm 1.96 (-15)^{\text{b,c}}$
297	14.0	3.4	31.9	659	17	10	$7.41 \pm 1.74 (-15)^{\text{c}}$
297	14.0	3.4	31.9	466	17	20	$4.30 \pm 1.01 (-15)^{\text{c}}$
297	14.0	3.4	31.9	450	17	20	$4.53 \pm 1.07 (-15)^{\text{c}}$
481	14.9	2.2	14.8	118	33	20	$2.82 \pm 0.64 (-14)^{\text{d}}$
493	35.6	5.2	11.7	302	14	20	$1.33 \pm 0.21 (-14)^{\text{d}}$
494	35.6	5.2	22.8	430	14	10	$1.43 \pm 0.23 (-14)^{\text{d}}$
705	11.9	1.2	2.6	386	89	20	$1.20 \pm 0.32 (-13)^{\text{c}}$
708	27.2	2.8	2.6	207	39	20	$9.98 \pm 1.68 (-14)^{\text{c}}$
737	12.0	1.2	5.6	321	92	10	$1.23 \pm 0.32 (-13)^{\text{c}}$
746	26.9	2.6	4.0	262	41	10	$1.21 \pm 0.20 (-13)^{\text{c}}$
760	27.2	2.6	3.1	214	22	20	$9.13 \pm 1.56 (-14)^{\text{c}}$

a)  $\sigma_T / T = \pm 2\%$ .

b) Should be read as  $(8.34 \pm 1.96) \times 10^{-15}$ .

c) BO from the B + O + M reaction.

d) BO from the B + SO<sub>2</sub> reaction.

**Table 3. Summary of HTP Upper Limit Determinations on BO + CO<sub>2</sub>**

$T^a$ (K)	$P$ (mbar)	$[M]$ ( $10^{18} \text{ cm}^{-3}$ )	$[\text{CO}_2]_{\text{max}}$ ( $10^{16} \text{ cm}^{-3}$ )	$F$ (mJ)	$\bar{v}$ ( $\text{cm s}^{-1}$ )	$z$ (cm)	$k_{\text{upper limit}}^b$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
298	169	3.24	11.2	20	16.2	10	1.5(-14) <sup>c</sup>
298	213	1.74	9.2	20	23.5	11.5	3.9(-14)
298	186	2.22	4.6	20	16.9	11.5	5.1(-15)
570	189	2.35	4.3	20	24	11.5	1.0(-14)
860	173	1.75	5.2	20	25	10	4.0(-15)
870	266	2.07	7.7	20	22	5	9.6(-15)

a)  $\sigma_T / T = \pm 2\%$ .

b) Equals  $2\sigma_{\text{kpsl}} / [\text{CO}_2]_{\text{max}}$

c) Should be read as  $1.5 \times 10^{-14}$ .

Table 4. Summary of HTFFR Upper Limit Determinations on BO + CO<sub>2</sub><sup>a</sup>

$T^b$ (K)	$P$ (mbar)	$[M]$ ( $10^{17} \text{ cm}^{-3}$ )	$[\text{CO}_2]_{\text{max}}$ ( $10^{15} \text{ cm}^{-3}$ )	$F$	$\bar{v}$ ( $\text{m s}^{-1}$ )	$z$ (cm)	$k_{\text{upper limit}}^c$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
782	5.8	7.16	4.81	131	67	10	$2.2(-14)^d$
787	5.8	7.12	4.78	158	67	20	9.1(-15)
982	8.2	8.07	4.99	176	65	20	8.6(-15)
982	8.2	8.07	4.99	146	65	20	1.4(-14)
1003	12.4	19.1	2.26	232	34	20	4.0(-14)
1011	7.2	6.88	1.48	74	51	20	2.7(-14)
1028	8.2	7.70	4.76	138	68	20	4.7(-15)
1028	13.8	13.0	8.02	133	40	20	9.6(-15)
1031	20.0	18.7	4.03	43	19	20	1.3(-14)
1193	7.0	5.7	0.81	77	93	20	2.5(-13)

a) BO from the B + O + M reaction.

b)  $\sigma_T / T = \pm 2\%$ .

c) Equals  $2\sigma_{\text{kpsl}} / 0.8[\text{CO}_2]_{\text{max}}$

d) Should be read as  $2.2 \times 10^{-14}$ .

## Figure Captions

1. Diagram of the High-Temperature Fast Flow Reactor (HTFFR) used for the BO reactions with HCl and CO<sub>2</sub>.

inlet A - NO, inlet B - 1 ppm B<sub>2</sub>H<sub>6</sub> and 2000 ppm N<sub>2</sub> in Ar, inlet C - HCl or CO<sub>2</sub>

or

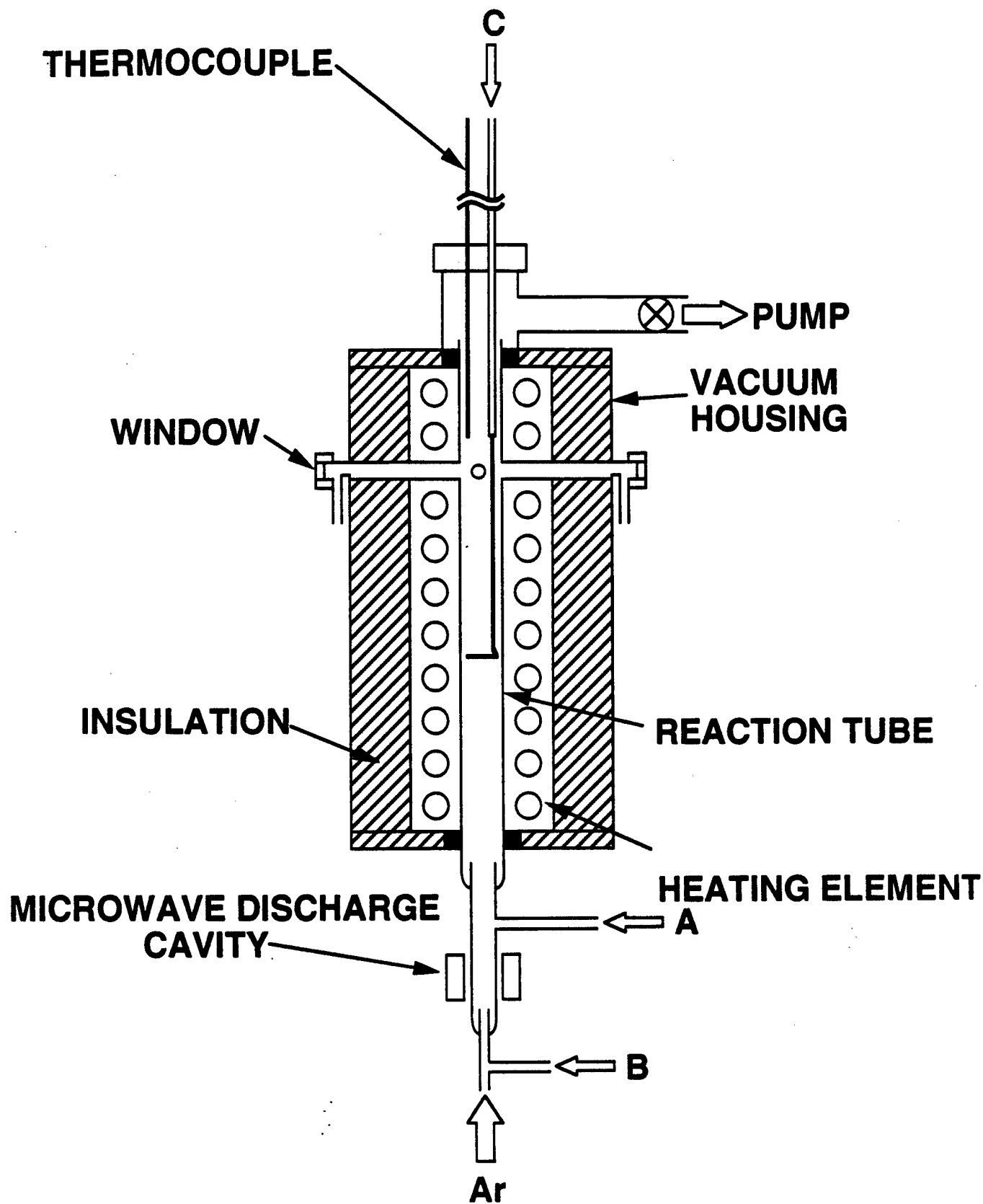
inlet A - SO<sub>2</sub>, inlet B - 2 ppm B<sub>2</sub>H<sub>6</sub> in Ar, inlet C - HCl

2. Plot of rate coefficient measurements for BO + O<sub>2</sub>.

- present work
- Stanton et al. [8]
- best fit expression to both data sets, eqn. (6)

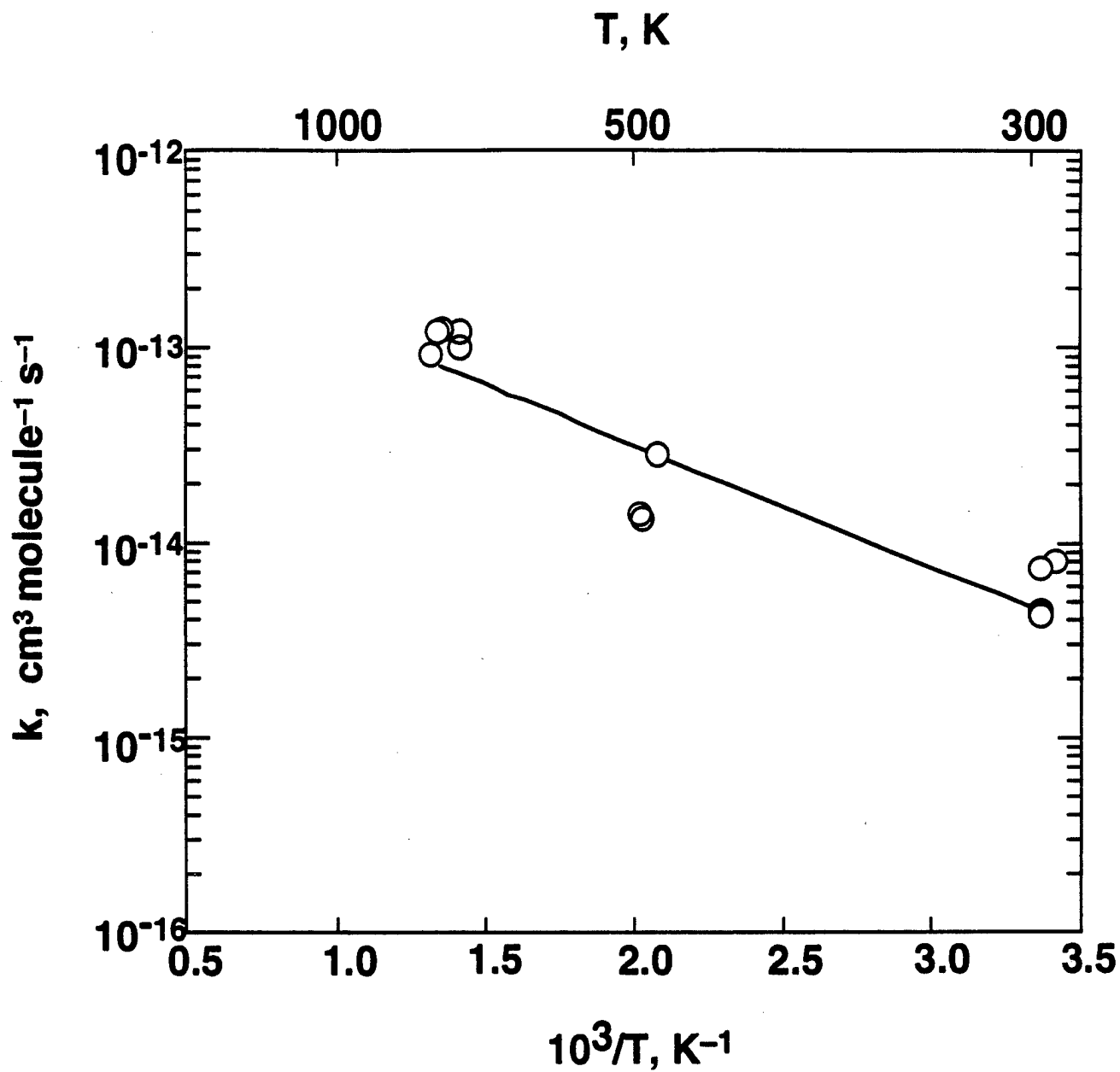
3. Plot of rate coefficient measurements for BO + HCl.

- present work
- best fit expression, eqn. (9)



Belyung, ..., and Fontijn **FIGURE 1**





Belyung, ..., and Fontijn

FIGURE 3