To aid in the development of boron-enhanced fluoro-nitramino explosives, the kinetics of individual reactions from those systems are investigated over wide temperature ranges. For $\text{BO} + \text{O}_2 \rightarrow \text{BO}_2 + \text{O}$ the measurements agree with earlier observation in the 400 - 1000 K range. No reaction could be observed between BO and CO$_2$ from 780 to 1200 K, indicating $k$ less than $1 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. For $\text{BO} + \text{N}_2\text{O} \rightarrow \text{BO}_2 + \text{N}_2$ $k(305-920 \text{ K}) = 3 \times 10^{-13}\exp(-1310 \text{ K/T})$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was obtained.
PROGRESS

Our goals are:

(i) 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

(ii) to use the measurements to obtain a further understanding, to allow predictions for additional reactions occurring with such explosives.

The measurements are made by laser-induced fluorescence, LIF, in high temperature reactors. Our efforts in this first year have concentrated on the development of methods for introducing BO in HTFFRs (high-temperature fast-flow reactors). A large number of methods were investigated. The best are: i) those by which B atoms are produced in a microwave discharge, followed by reaction with O atoms or SO₂, and ii) those where LiBO₂, HBO₂, or B₂O₃ are vaporized and passed through a microwave discharge. However, all led to rate coefficients somewhat decreasing with residence time. This appears to be due to rapid wall dimerization of BO. Nonetheless, we obtained measurements on BO + O₂ → BO₂ + O between 400 and 1000 K. These are in essential agreement with earlier measurements¹ on this reaction of k(300-1000 K) = 7.0x10⁻¹²exp(255 K/T) cm³molecule⁻¹s⁻¹. There a reactor fashioned after our real-time MHTP (metals high-temperature photochemistry) apparatus was used. Since further BO reactions show the same problem, we will use the HTFFR to determine approximate rate coefficients and make accurate measurements in the MHTP apparatus, which provides a wall-less reaction environment. The HTFFR equipment is still required for measurements from about 1000 to 1800 K, where the BO production method developed¹ for the photo-initiated reaction can not be used.

Two sets of such approximate measurements have already been made. The first of these is for the BO + CO₂ → BO₂ + CO reaction. While at room temperature a slow pressure-dependent reaction was observed, from 780 to 1200 K (the highest temperature explored thus far) no reaction was found. This indicates rate coefficient values less than about 1 x 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹. This is four orders of magnitude
lower than obtained for the \( \text{BO} + \text{O}_2 \) reaction. Even more importantly, it is two to four orders of magnitude lower than the guesstimated values in the current models.\(^2\)\(^-\)\(^4\)

While the \( \text{BO} + \text{CO}_2 \) reaction and its reverse are considered to be highly sensitive for boron combustion in hydrocarbon systems,\(^2\)\(^,\)\(^3\) they are not regarded so for the envisioned fluoro-nitramino based explosives.\(^4\) However, such a large difference is important for those as well, once again illustrating the importance of measurements for the development of realistic models.

The measurements on the \( \text{BO} + \text{N}_2\text{O} \rightarrow \text{BO}_2 + \text{N}_2 \) reaction have yielded
\[ k(305-920 \text{ K}) = 3 \times 10^{-13} \exp(-1310 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}. \]

**PLANS**

Preparations for work on the \( \text{BO} + \text{HCl} \) and \( \text{BF}_3 \) reactions have started. Once those measurements have been made below \( \sim 1200 \text{ K} \), work on this reaction and the \( \text{O}_2 \) and \( \text{CO}_2 \) reaction above \( \sim 1200 \text{ K} \) in the HTFFR will start. (The \( \text{N}_2\text{O} \) study is restricted to the \( 920 \text{ K} \) limit because of thermal instability.) For such higher temperature work \( \text{BO} \) LIF measurements will be made at shorter wavelengths, to reduce potential wall radiation interference.

We also plan to test the compatibility of our reactor materials with HF at high temperatures for measurements with that crucial reactant. For the study of the other boron species of ONR interest, \( \text{BO}_2 \) and \( \text{BF} \), no similar problems as encountered with \( \text{BO} \) are expected and the HTFFR technique will, at least initially, be used for their study. Additionally to the above two high-temperature techniques, where laser-induced fluorescence is used for monitoring of the boron species, our HTFFR-mass spectrometer will be used for product identification. Especially product \( \text{OBF} \) detection would be important.

**PARTICIPANTS AND CONTACTS**

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PUBLICATIONS AND AWARDS

None this year.

REFERENCES


