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To aid in the development of boron-enhanced fluoronitramino explosives, the kinetics of individual reactions are measured over wide temperature ranges. Using the HTFFR technique it was established that, for BO + HCl → OBCl + H, k (300-760 K) = $5.7 \times 10^{-13} \exp(-1437\ K/T) cm^3 molecule^{-1} s^{-1}$. Currently this determination, and HTFFR results on the BO reactions with O_2, CO_2 and N_2O, are being checked with an MHTP reactor.

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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.

Our efforts this past year have concentrated on completing the series of experiments on BO reactions in a high-temperature fast-flow reactor (HTFFR) and preliminary experiments on reactions of this species in a metals high-temperature photochemistry (MHTP) reactor. Additionally, a series of experiments was undertaken to test the ability of our reactors to withstand HF at high temperatures, in preparation for studies with this reactant; no problems were encountered. However, it was found desirable to protect the vacuum pump with a CaO trap, and for work with BF and BF_3, additionally with an activated carbon trap.

Previously, in the HTFFR study of the BO + O_2 reaction, unusually wide scatter in the rate coefficients was encountered.[1] As earlier work in a reactor, fashioned after our MHTP reactors, had not shown such scatter,[2] this suggested to do further work on this reaction using that approach, following some further HTFFR studies. The additional BO reactions thus studied this year were BO + HCl and N_2O. Of these the first did not show appreciable scatter, but with the second the scatter was again unsatisfactorily high. We obtained, in units of cm^3 $molecule^{-1}$ s^{-1},

(1) $BO + HCl \rightarrow OBCl + H \quad \Delta H = -5.7 \pm 37$ kJ mol^{-1}
k_1 (300-760 K) = 5.7×10^{-13} exp(-1437 K/T)

(2) $BO + N_2O \rightarrow BO_2 + N_2 \quad \Delta H = -367$ kJ mol^{-1}
k_2 (300-1000 K) = 3×10^{-13} exp(-1310 K/T)

where our confidence is considerably higher in the first than in the second result. Checks on both reactions will be conducted in the HTP reactor this coming year. Presumably, less effort there will have to be expended on the first than on the second reaction.

Currently, we are engaged in re-measuring the reaction

(3) $BO + O_2 \rightarrow BO_2 + O$

in the HTP facility. After that, and extending into the proposed contract extension period, we will check the HTFFR result[1] that

(4) $BO + CO_2 \rightarrow BO_2 + CO$

has rate coefficients of less 1 x 10^{-15} over the 780-1200 K temperature range. This is our result that has thus far the most direct impact on current models,[3] as it is some three orders of magnitudes slower than guessed in those models.

The proven methods to produce BO in the HTP reactor is the photolysis of $BCl_2(OCH_3)$, which appears to be good up to around 1000 K.[2,4] We are also considering another method referenced in the same articles. That method is photolysis of a boron compound such as BCl_3 to produce B atoms, followed by BO production from their reaction with an oxidant such as O_2. It has been observed to suffer from interference from vibrational relaxation, but would have the advantage of allowing work at much higher temperatures, at least 1400 to 1500 K. The problem in previous work with this production method was that vibrational relaxation occured on the same time scale as the reaction, when narrow beam laser-induced fluorescence was used. However, by using a cw flowlamp, or an expanded laser beam, the time scale of MHTP experiments can be increased by several orders of magnitude,[5] and a vibrational relaxation agent, such as SF_6, may help further.

PLANS

Our reaction selection will continue[1] to be based on the Aerodyne-Princeton modeling work[3] and checks thereof. As a result of discussions at the June 1995 Boron Combustion Workshop, on the work of Drs. Mike Page and Maribel Soto, we have now removed BF + HF from the list, while BF + H_2O has increased in importance. Thus in addition to reactions (1) - (4) above, the list for study, discussed last year, now looks as follows, in the approximate sequence planned for study:

$BO + N_2O$, HF, BF_3, H_2O
$BF + H_2O$, O_2, BF_3,
$BO_2 + N_2O$
$F + H_2O$

PARTICIPANTS AND CONTACTS

The experimental work has been performed by G.T. Dalakos with help from D.P. Belyung. In addition to these two students, W.F. Flaherty, our group technician, has participated. We thank Dr. R.A. Yetter for several informative discussions.

PUBLICATIONS AND AWARDS

None this year.

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