**Title:** Advanced B and Al Combustion Kinetics Over Wide Temperature Ranges

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**Abstract:**

To help provide a better understanding of reliable input data on gas-phase combustion reactions of B and Al species, experimental measurements were made in a high-temperature fast-flow reactor. The following rate coefficient expressions were obtained (in cubic cm, per molecule, per second units): $\text{BC}_2 + \text{O}_2 \rightarrow \text{Products}, \; 2.2 \times 10^{-11} \; \text{exp}(-4620 \; \text{K}/\text{T})$; $\text{BC}_2 + \text{CO}_2 \rightarrow \text{OBC}_2 + \text{CO}, \; 6.7 \times 10^{-13} \; \text{exp}(-4500 \; \text{K}/\text{T})$. A comparison was made to similar reactions involving Al species, reported last year. The radiative lifetime of AlC (A one pie), of importance to plume models, was determined to be 6.4 ns.
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I. RESEARCH OBJECTIVES

Current ability to improve the combustion efficiency of B and Al solid propellants and slurries is hampered by a lack of understanding and knowledge of the kinetics of the individual reactions involved and the ways and manner by which temperature affects the rate coefficients and product channels. While the simple Arrhenius-type equation $k(T) = A \exp\left(-\frac{E_A}{RT}\right)$ has over limited temperature ranges been of great value, when applied to wide temperature ranges it is often not obeyed. Particularly for exothermic and slightly endothermic reactions, order of magnitude errors can be made by extrapolations based on the Arrhenius equation. It is the goal of this program to provide an insight in the kinetic behavior of B and Al radical oxidation reactions as influenced by temperature. To this end measurements are made in high-temperature fast-flow reactors (HTFFR). These unique tools provide measurements on isolated elementary reactions in a heat bath. With traditional high-temperature techniques, such as flames and shock tubes, such isolation is usually impossible to achieve; as a result, data on any given reaction depend on the knowledge of other reactions occurring simultaneously, leading to large uncertainties. HTFFRs allow kinetic studies from room temperature up to about 2000 K to provide wide range $k(T)$ (temperature-dependent rate coefficient) data.

In the work performed thus far under this grant laser-induced fluorescence LIF has been used to monitor reactant concentrations. The objectives of that work are to measure, over the widest achievable temperature ranges, the kinetics of:

i) $Al$, $AlCl$ and $BCl$ oxidation reactions, and

ii) oxidation reactions of other simple Al and B-containing radicals, such as $AlO$ and $BO$. 
Most tri-atomic products of the oxidation reactions of these monoxides and monohalides have no identified electronic transition spectra and cannot be detected by LIF. To unambiguously establish the kinetics of reactions involving these triatomics and ultimately to develop a good understanding of the reactions leading to the final combustion products, $\text{Al}_2\text{O}_3$ and $\text{B}_2\text{O}_3$, we have constructed an HTFFR with mass spectrometer detection. This instrument is currently being tested. The first objectives for the work with that apparatus are:

(i) to identify the products of the $\text{AlCl} + \text{O}_2$ and $\text{BCl} + \text{O}_2$ reactions, discussed in Section II, and to determine the temperature dependence of the branching ratio of the $\text{AlO}_2$ and $\text{OAlCl}$ product channels of the former reaction, and

(ii) to resolve the large discrepancy between $\Delta H_f(\text{AlO}_2)$ derived from HTFFR-LIF observations and from Knudsen cell mass spectrometry experiments.$^2,^3$

II. STATUS OF THE RESEARCH EFFORT

In the first year of this grant we have made measurements on several reactions involving $\text{AlCl}$. The $k(T)$ data obtained have been reported in the preceding annual report. As an additional Al-study, we have measured the previously unknown radiative lifetime of $\text{AlCl} \, 1\Pi$ to be 6.4 ns. This latter result has already been incorporated in rocket plume uv band model calculations made at Aerodyne.$^4$ Most of this $\text{AlCl}$ work has now been written up and published;$^5^-^7$ a paper on the $\text{Al} + \text{Cl}_2$, $\text{Al} + \text{HCl}$ and $\text{AlCl} + \text{Cl}_2$ reactions is in preparation. In Figure 1 the $\text{AlCl} \, k(T)$ data are compared to results from our previous aluminum oxidation studies involving oxygen oxidizers.$^8$

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* We plan to "complete" this figure by making measurements on the $\text{AlO} + \text{Cl}_2$ and $\text{AlO} + \text{HCl}$ reactions.
Figure 1 Summary of HTFFR Rate Coefficient Measurements on Al/O/Cl Reactions
Together these illustrate the variety of $2\pi k$ vs. $T^{-1}$ dependences observed, the wide range of rate coefficient data that can be measured and the wide range of temperatures that can be covered.

A major breakthrough occurred in the present year when we developed a method for reproducibly introducing a boron species, BCl, into an HTFFR*. This method, production of BCl by passing $B_2H_6/Ar/Cl_2$ or HCl mixtures through a microwave discharge is illustrated in Figure 2. It has led to the following results:

\[
\begin{align*}
(1) \quad & \text{BCl} + O_2 \quad \text{T = 540 to 1670 K} \\
& \text{BO}_2 + Cl \\
& k_1 = 2.2 \times 10^{-11} \exp(-4620 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\
(2) \quad & \text{BCl} + CO_2 \rightarrow \text{OBCl} + CO \\
& \text{T = 770 to 1570 K} \\
& k_2 = 6.7 \times 10^{-13} \exp(-4500 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\end{align*}
\]

The study of reaction (1) has already been accepted for publication,\textsuperscript{10} that of reaction (2) will be written up together with the results from the BCl $+ Cl_2$ reaction, now being studied.

In Figure 3 the BCl $+ O_2$ data are compared to our results\textsuperscript{5} on the AlCl $+ O_2$ reaction and those of an earlier study of the BF $+ O_2$ reaction over a more limited temperature range (675 to 1035 K).\textsuperscript{11} Two observations should be made:

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* Our previous attempts at BCl production, such as reactive vaporization by passing BCl$_3$ or Cl$_2$ over solid B at T $\geq$ 1100 K,\textsuperscript{9} led to kinetic data which were a function of reactor parameters.
Figure 2 Schematic of the HTFFR in use for the LIF Studies of BCl\(_2\) Reactions

![Schematic Diagram]

Ar + B\(_2\)H\(_6\) + Cl\(_2\)

Figure 3 Comparison of the \(k(T)\) Data of the BCl\(_2\) + O\(_2\), AlCl\(_3\) + O\(_2\) and BF + O\(_2\) Reactions

- BCl\(_2\) + O\(_2\)
- AlCl\(_3\) + O\(_2\)
- BF + O\(_2\)
(i) In the temperature range covered the BCl reaction is faster than the AICl reaction and considerably faster than the BF reaction. The latter could have important consequences for advanced propellants where fluorine would be a principal species; a similar comparison between the AICl + O2 and AIF + O2 reactions would appear to be significant for a future HTFFR study.

(ii) Figure 3 shows that while the AICl + O2 reaction has a sharply curved Arrhenius plot above ≈ 1000 K, the BCl + O2 reaction displays no noticeable deviation from linear \( \ln k \) vs. \( T^{-1} \) (normal Arrhenius) behavior. We have speculated that the AICl plot indicates a transition from an \( \text{AlO}_2 + \text{Cl} \) product channel at the lower temperatures to \( \text{OAICl} + O \) at the higher temperatures. The straight line for BCl + O2 suggests that only one channel is operative (one type of product is formed). If this were \( \text{OBCl} \), the equivalent of the postulated high-temperature \( \text{Al} \) product, the shape of the two plots would suggest that they may cross, i.e., that at very high temperatures the AICl reaction could be faster than the BCl reaction. However, if the BCl product is \( \text{BO}_2 \), the equivalent of the lower temperature \( \text{Al} \) product, a very fast BCl + O2 reaction may be indicated at high temperatures as sharp upward curvature in the BCl + O2 plot, similar to that of AICl + O2, would then be a reasonable expectation. Our planned mass spectrometer experiments on the AICl + O2 and BCl + O2 reactions would provide product identification and hence should decide between these possibilities.
In Figure 4 we compare the measured rate coefficients of the \( \text{BCl} + \text{CO}_2 \) reaction (2) to those we obtained\(^6\) for

\[
(3) \quad \text{AlCl} + \text{CO}_2 \rightarrow \text{OAlCl} + \text{CO}
\]

\[
k_3 = 2.5 \times 10^{-12} \exp(-7550 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

On thermochemical grounds the products given in Eqs. (2) and (3) are the only possible. While the Al reaction is the slower at the measured temperatures, extrapolation suggests that above about 2300 K it would be the faster reaction.

![Figure 4](image_url)

**Figure 4** Comparison of the \( k(T) \) Data of the \( \text{BCl} + \text{CO}_2 \) and \( \text{AlCl} + \text{CO}_2 \) Reactions
Our measurements on

\[(4) \quad \text{BCl} + \text{Cl}_2 \rightarrow \text{BCl}_2 + \text{Cl} \]

now in progress, suggest a rate coefficient at 500 K about half that of

\[(5) \quad \text{AICl} + \text{Cl}_2 \rightarrow \text{AICl}_2 + \text{Cl} \]

with only a small temperature dependence for either reaction, compare Figure 1. One of our long-term goals is to obtain comparisons of B-species reactions to most of the A\text{2} reactions shown in that figure; in other words, to prepare for B-species reactions a comprehensive data compilation similar to Figure 1.

III. CUMULATIVE LIST OF PUBLICATIONS


IV. PROFESSIONAL PERSONNEL

Donald F. Rogowski and Aleksander G. Slavejkov performed the experimental work discussed in Section II. The former is expected to receive his Ph.D. in the near future. His research has been fully supported by AFOSR. Various people in our research group, particularly David A. Stachelczyk and William F. Flaherty, have been involved in the construction and testing of the mass-spectrometer-HTFFR apparatus.

V. PRESENTATIONS AND OTHER INTERACTIONS

We presented papers and seminars in which results of our AFOSR-sponsored work were discussed, at the:

1. Department of Chemistry, University of Toronto, Toronto, Ont. (May 1986).
3. AFOSR/ONR Contractors Meeting on Combustion, Stanford University, Stanford, CA (June 1986).
6. Department of Applied Mechanics and Engineering Sciences, University of California at San Diego, La Jolla, CA (October 1986).
7. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD (May 1987).
9. AFOSR/ONR Contractors Meeting on Combustion and Rocket Propulsion, Pennsylvania State University, University Park, PA (June 1987).
11. Chemical Thermodynamics Division, National Bureau of Standards, Gaithersburg, MD (November 1987).


Dr. C.W. Larson of the Air Force Astronautics Laboratory, and other Air Force Personnel, contacted us several times in 1986 and 1987 to discuss the design of a high-temperature reactor for use in spectroscopic measurements on hydrogen/metal-vapor mixtures. They are interested in such information in the context of the Solar Plasma Propulsion Program. We maintain periodic contacts with Dr. David P. Weaver of that laboratory. Dr. J. Lurie, of Aerodyne Research Inc., called us to obtain information on our AXCI radiative lifetime measurements for their plume model calculations for AEDC. Dr. M.W. Chase of the National Bureau of Standards had several discussions with us on the implication of our measurements for entries on aluminum species in the JANAF Thermochemical Tables. We have initiated some collaboration with Dr. J.R. McDonald's group at N.R.L., in connection with their BH compound combustion research and our mass spectrometric work. I (A.F.) have accepted an invitation to serve as a member of the ONR Board of Visitors for review of their Mechanics Division Program.

VI. REFERENCES


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