To help provide a better understanding of the temperature dependence of the kinetics of diatomic metal radical oxidation reactions, experimental measurements have been made in the 450 to 1750 K temperature regime. An HTFFR (high-temperature fast-flow reactor) has been used. The metal radical concentrations were measured by laser-induced fluorescence. The general uses of this spectrometric technique for rate measurements on reactants and products, as well as for product species identification and product state determination, are reviewed.

The radicals studied in the HTFFR on this grant are \( \text{A}_2\text{O}_x \), \( \text{A}_2\text{C}_x \) and \( \text{BC}_x \).

Production methods for these are discussed. For the reaction...
\[ \text{We obtain } k(T) = 2.5 \times 10^{-14} \exp(400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]

This negative activation energy implies \( D(\text{O-} \text{AsO}) > D(\text{O-CO}) = 530 \text{ kJ mol}^{-1} \), which is in apparent disagreement with the \( \text{OAsO} \) dissociation energy obtained for \( \text{AsO}_2 \) from \( \text{AsO}_3 \) evaporation-mass spectrometry studies. It is argued that the latter \( \text{AsO}_2 \) may have a different structure from that of the present work. For the reaction between \( \text{AsCl}_2 \) and \( \text{O}_2 \) we find \( k(T) = 6.8 \times 10^{-13} \exp(-2990/T) + 1.5 \times 10^{-10} \exp(-10600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), which is compatible with a mechanism where the \( \text{AsO}_2 + \text{Cl}_2 \) product channel dominates at lower temperatures, while the \( \text{OAsCl}_2 + \text{O} \) channel dominates at higher temperatures. The \( \ln k(T) \) versus \( 1/T \) dependence of the \( \text{AsCl}_2/O_2 \) reaction is contrasted to those observed for the \( \text{AsO}/O_2 \) and \( \text{BF}/O_2 \) reactions. Quantitative results on \( \text{BC}_2 \) have not yet been obtained due to a reaction between this radical and the \( \text{AsO}_3 \) of the reactor wall. However, a possibly favorable effect of chlorine on boron slurry combustion initiation is indicated by this work.
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MATTHEW J. KEPER
Chief, Technical Information Division
I. RESEARCH OBJECTIVES

Current ability to improve the combustion efficiency of metallized propellants is severely hampered by a lack of understanding, and knowledge, of the manner by which temperature affects the rate coefficients of individual reactions and reaction channels. While the simple Arrhenius equation

\[ k(T) = A \exp(-E_a/RT) \]

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. In earlier work we had primarily concentrated on measuring and interpreting the kinetics of metal atom oxidation reactions over wide temperature ranges. The goal of the present program was to begin to provide a similar insight in the kinetic behavior of metal monoxide and monohalide radical oxidation reactions.

Figure 1 shows some of the reactions of interest and their relevance to advanced propulsion systems development. It also gives a schematic of the HTFFR, high-temperature fast-flow reactor, method we used to generate the metallic radicals and measure their oxidation kinetics. This unique tool, suitable for the 300 - 1900 K temperature range, provides 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.

The ultimate results of the current work with this apparatus were to be:

(i) Wide T-range \( k(T) \) expressions for a number of metallic radical oxidation reactions, and

(ii) Based on (i), an improved understanding of the chemistry which governs the temperature dependence of such reactions.
HIGH TEMPERATURE COMBUSTION KINETICS OF METALS

SCIENTIFIC APPROACH

GOALS

- UNDERSTAND THE MECHANISMS OF METALLIC RADICAL OXIDATION REACTIONS.
- MEASURE REACTION RATE COEFFICIENTS FOR REACTIONS IMPORTANT TO ADVANCED PROPULSION SYSTEMS:
  - BC\textsubscript{6} + O\textsubscript{2} \rightarrow Emissions from Air Breathing Missile Plume After Burning
  - Al\textsubscript{2}O\textsubscript{3} + CO\textsubscript{2} \rightarrow Combustion of Aluminized Composite Propellants
  - BO + O\textsubscript{2} \rightarrow Combustion of Boron Slurries
  - AlC\textsubscript{2} + O\textsubscript{2} \rightarrow Microparticulates Formation
  - AlF + O\textsubscript{2} \rightarrow Tendency of Fluorinated Binders to Reduce Agglomeration
- OBTAIN THESE \( A(T) \) DATA OVER THE 300-2,000 K RANGE. NON-ARRHENIUS BEHAVIOR PRECLUDES EXTRAPOLATION FROM NARROW TEMPERATURE INTERVALS.

TECHNIQUE

High-Temperature Fast-Flow Reactor

![Diagram of high-temperature fast-flow reactor](image)

\[ \text{Al} + \text{CO}_2 \rightarrow \text{AlO} + \text{CO} \text{ (FAST)} \]
\[ \text{AlO} + \text{CO}_2 \rightarrow \text{AlO}_2 + \text{CO} \text{ (SLOW)} \]

Fig. 1
II. RESULTS

A. Cumulative Chronological List of Publications and Their Abstracts


2. A. Fontijn and R. Zellner, "Influence of Temperature on Rate Coefficients of Bimolecular Reactions," in ibid., Chap. 1.*


   The uses of laser-induced florescence (LIF) for rate measurements on reactants and products, as well as for product species identification and product state determination, are illustrated by the use of examples. LIF studies discussed are preferentially chosen from work on single reactions at elevated temperatures. LIF is compared to other techniques for observations on combustion intermediates. Reactions of refractory species are treated, followed by reactions of 0 and OH with hydrocarbon molecules and some reactions of other radicals formed in flames. Finally, some work on reactions of vibrationally and electronically excited species is reviewed. Extensive literature references are provided for detail.


   The dependence of the rate coefficients of gas-phase oxidation reactions of metallic species on temperature is discussed. Examples given pertain primarily to A7 and B species reactions in the 300 - 1900 K range. These reactions show a wide variety of in k(T) vs. T-1 behavior patterns. It is argued that, because of this variety, it is not yet possible to make reliable predictions regarding reactions for which no experimental data on temperature dependence are available. However, some guidance is given toward making preliminary estimates. Quantitative kinetic data on the discussed reactions are given. The experimental method (HTFFR) used to obtain these data is briefly reviewed.

*Contains no abstract

The title reaction has been studied in a high-temperature fast-flow reactor (HTFFR) at temperatures from 500 to 1300 K. Laser-induced fluorescence was used to monitor relative $[\text{AtO}]$. $k(T)$ was determined to be $(2.5 \pm 1.3) \times 10^{-14} \ exp\ [(400 \pm 280)/T] \ cm^3 \ molecule^{-1} \ s^{-1}$ (confidence level > 95%). The reaction probably proceeds via an intermediate complex which preferentially dissociates to the reactants. The negative activation energy implies $D(\text{O-AtO}) > D(\text{O-CO}) = 530 \ kJ \ mol^{-1}$, which is incompatible with the O-AtO dissociation energy obtained for AtO$_2$ from Al$_2$O$_3$ evaporation-mass spectrometry studies. It is argued that the latter AtO$_2$ may have a different structure from that of the present work.


The dependence of the rate coefficients of gas-phase oxidation reactions of monatomic and diatomic refractory species on temperature is discussed. Examples given pertain primarily to At and B species reactions in the 300 - 1900 K range. These reactions show a wide variety of $k(T)$ vs. $T^{-1}$ behavior patterns. It is shown that, because of this variety, it is not yet possible to make reliable predictions regarding reactions for which no experimental data on temperature dependence are available. However, some guidance is given toward making preliminary estimates. Quantitative kinetic data on the reactions are given and the importance of their thermochemistry is discussed. The experimental method (HTFFR) used to obtain these data is briefly reviewed.


A method for the production of $\text{AlCl}$ radicals in an HTFFR (high-temperature fast-flow reactor) is described. Their relative concentration in the title reaction is monitored by laser-induced fluorescence. The overall

*Work completed under Grant 86-0019
reaction rate coefficients can be fitted by the expressions
\[ k(T) = 6.84 \times 10^{-13} \exp(-2990/T) + 1.53 \times 10^{-10} \exp(-10600/T) \]
and
\[ k(T) = 1.94 \times 10^{-27} T^{4.39} \exp(261/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]
Error limits are described in the text. The results are shown to be compatible with a mechanism where the A\(_2\)O\(_2\) + Cl product channel dominates at lower temperatures, while the OAtC\(_x\) + O channel dominates at higher temperatures. The \( \ln k(T) \) versus \( T^{-1} \) dependence of the A\(_2\)C\(_x\)/O\(_2\) reaction is contrasted to those observed for the A\(_2\)O/O\(_2\) and BF/O\(_2\) reactions.

B. Some Illustrative Discussion

Some of the results from the publications given above are illustrated in Fig. 2. The A\(_2\)C\(_x\)/O\(_2\) reaction has a \( \ln k \) versus \( T^{-1} \) plot with gradual curvature, somewhat similar to that observed in many reactions between hydrocarbon molecules and OH radicals, but different from any plot observed in previous metallic species oxidation reactions.\(^1\)\(^-\)\(^3\) The interpretation of this behavior is that of two competing reactions dominating in different temperature regimes.\(^4\) Since the electronic spectra of the probable products OAtC\(_x\) and A\(_2\)O\(_2\) are not known, laser-induced fluorescence, the diagnostic used in the present work, is unsuited to their identification. Under a new grant we are building an HTFFR with mass spectrometer detection, which should allow us to identify reaction products such as these tri-atomic species -- additionally their further reactions should be observable with the mass spectrometer.

The second reaction in Fig. 2, A\(_2\)O/CO\(_2\), shows a sharply different behavior. It has a slight negative activation energy, indicative of the formation of an intermediate reaction complex which preferentially dissociates to the original reactants, rather than to products.\(^5\) The kinetic behavior of this reaction also contrasts sharply from that of the A\(_2\)/CO\(_2\) reaction, which is also illustrated in Fig. 2. That reaction obeys the Arrhenius equation from 300 to 700 K, i.e. a straight line \( \ln k \) vs. \( T^{-1} \) plot is obtained. Above 700 K \( k \) rises sharply with increasing \( T \). This behavior can be explained by the increase in the thermal population of CO\(_2\) in bending vibrational modes.\(^1\)\(^,\)\(^6\) The latter have, contrary to ground state linear CO\(_2\), a finite electron affinity. This allows them to react with metal atoms, such as A\(_2\), by an electron
ACCOMPLISHMENTS

OBSERVATION

\[ k = 8 \times 10^{-13} \]

\[ \text{AtCl} + \text{O} \]

DOMINATES AT HIGH TEMPERATURES

\[ \text{Al} + \text{CO} \rightarrow \text{AlO} + \text{CO} \]

DOMINATES AT LOW TEMPERATURES

\[ k = 2 \times 10^{-15} \]

INTERPRETATION

\[ k_{\text{observed}} = \frac{k_1}{k_2} \]

\[ \text{AlO} + \text{CO}_2 \rightarrow \text{AlCO}_3 \rightarrow \text{AlO}_2 + \text{CO} \]

\[ 1750K \]

\[ 1300K \]

negative T-dependence

\[ 1900K \]

\[ 1900K \]

\[ \text{Al} + \text{O} = \text{C} = \text{O}(\nu = 0) \rightarrow \text{AlO} + \text{CO} \]

\[ \text{THERMAL} \]

\[ \text{Al} + \text{CO} \rightarrow \text{AlO} + \text{CO} \]

\[ k = 4 \times 10^{-11} \]

\[ 700K \]

\[ 300K \]

\[ \text{Al} + \text{O} = \text{C} = \text{O}(\nu = 0) \rightarrow \text{AlO} + \text{CO} \]

\[ \text{THERMAL} \]

\[ \text{Al} + \text{O} = \text{C} = \text{O}(\nu = 0) \rightarrow \text{AlO} + \text{CO} \]

\[ k = 2 \times 10^{-13} \]

\[ \text{Al} + \text{CO} \rightarrow \text{AlO} + \text{CO} \]

\[ k = 2 \times 10^{-13} \]

\[ \text{Al} + \text{CO} \rightarrow \text{AlO} + \text{CO} \]

\[ k = 2 \times 10^{-13} \]

\[ \text{Al} + \text{CO} \rightarrow \text{AlO} + \text{CO} \]

\[ k \in \text{cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ \text{Al}_f \gg \text{Al}_0, \text{i.e. BENT CO}_2 \]

HAS MUCH LARGER REACTION CROSS SECTION THAN LINEAR CO\textsubscript{2}

Fig. 2
jump ionic mechanism which interaction takes place at larger internuclear
distances (and hence reaction cross sections) then the covalent interaction of
ground state CO₂. The absence of a similar dependence on the vibrational
excitation of CO₂ in the A₂O/CO₂ reaction can be attributed to the larger
ionization potential I.P. of A₂O (I.P. = 9.5 ± 0.5 eV) compared to A₂ (I.P. =
5.98 eV).

None of these results could have been predicted. This variety, as well
as that of our earlier observations on metal atoms,¹⁻³ demonstrates the
necessity to make experimental measurements on metallic species oxidation
reactions in order to arrive at an understanding of the kinetics of such reac-
tions. Many more reactions need studying to arrive at a meaningful predictive
ability.

C. Boron Species Observations

Considerable effort has been spent to produce BCₓ and study its reac-
tions. Those kinetic studies have not yet been successful, but information
was obtained which indicates approaches for future study. Additionally,
observations were made both regarding aspects of the initiation of boron
combustion and unjustified data interpretation in the literature on BCₓ pro-
duction.

According to Krenev et al.⁷ BCₓ can be produced in a flow tube by passing
BCₓ₃ over solid boron in the 1373 to 1573 K temperature regime. By flowing
BCₓ₃/Ar mixtures over B chunks at 1200 K we indeed observed strong laser-
induced fluorescence signals at 272 nm, corresponding to the A-X (0,0) tran-
sition of BCₓ. However, similar signals were observed when the boron was
removed. Thus the signals observed can largely be attributed to
BCₓ₃ dissociation. Since this process would continue in the reaction zone, a
method for BCₓ production involving BCₓ₃ is unsuitable for HTFFR kinetics
observations. We next produced BCₓ by passing Cₓ₂ over B chunks at 1100 to
1200 K, which also gave strong BCₓ signals. This method was used for studies
of BCₓ + O₂ kinetics.

Solid boron is covered by a boron oxide layer which effectively inhibits
boron combustion by oxygen at temperatures up to about 2000 K.⁸⁻¹⁰ The fact
that we were able to produce BC\(_2\) at much lower temperatures indicates that chlorine can penetrate the oxide layer to initiate reaction. Thus addition of chlorine compounds would appear one way to help initiate boron combustion in boron slurries.

Studies of the BC\(_2\)/O\(_2\) reaction led to rate coefficients which were a function of the distance between the O\(_2\) inlet and the observation port and of the average gas velocity. Hence these could not be interpreted in terms of the BC\(_2\)/O\(_2\) reaction kinetics. An investigation of the cause of this apparatus effect showed that (i) BC\(_2\) signals were produced when a reaction tube had been used for a while and the B chunks and C\(_2\)\(_2\) were removed, (ii) with B chunks and C\(_2\)\(_2\) present, but no added Al, strong LIF signals of Al\(_x\)Cl\(_x\) were observed and (iii) with a new reaction tube very strong BC\(_2\) signals were observed, which decreased rapidly in the first 15 to 20 minutes of operation. All of this indicates that boron chloride compounds react with the "mullite glass" Al\(_2\)O\(_3\)/SiO\(_2\) (McDanel MV 30) reaction tube walls and replace Al. Similar problems were not encountered when next we produced Al\(_x\)Cl\(_x\) by passing C\(_2\)\(_2\) over an Al wetted tungsten coil: kinetic studies of the Al\(_x\)Cl\(_x\) + O\(_2\) reaction yielded rate coefficients independent of the reaction tube distance and flow velocity used.\(^4\)

It still appears possible to study BC\(_2\) reactions with reaction tubes made of other wall materials or coated with a suitable compound. A quartz tube appears to be one possibility,\(^1\) but would restrict observations to temperatures less than about 1100 K. Pure (998 grade) alumina reaction tubes, used in earlier HTFFR studies, were found to be unsuitable as they were rapidly consumed by chlorine at high temperatures, while the MV 30 tube was found to be resistant to chlorine.\(^4\) The search for a reaction tube resistant to the simultaneous presence of boron compounds, chlorine and oxygen at high temperatures could advantageously be made with the HTFFR mass spectrometer apparatus (Section IIB). A mass spectrometer allows scanning over a wide range of masses (hence compounds) in one experiment. This can not be done with LIF, as each dye used there is specific for a narrow wavelength range; hence specific for one, or a few, compounds only.
III. PROFESSIONAL PERSONNEL

Two graduate students have been the principal associates in this work. Andrew J. English participated from December 1981 until May 1984. Most of his achievements have been described in his M.E. thesis entitled, "High-Temperature Fast-Flow Reactor for the Study of Metallic Radical Combustion Kinetics" (December 1983).

Donald F. Rogowski participated from January 1984 until the end of the grant. His principal achievements are in publications 5 and 7 of Section II A, above. Further details will be included in his Ph.D. thesis, which is scheduled for completion by May 1987. He also performed BCx experiments discussed in Section II C.

IV. CUMULATIVE CHRONOLOGICAL LIST OF PRESENTATIONS AND CONTACTS

Presentations on our work were given at the:

1. AFOSR/AFRPL Rocket Propulsion Research Meeting, Lancaster, CA (March 1982).
2. Departments of Chemistry and of Atmospheric and Oceanic Science, University of Michigan, Ann Arbor, MI (March 1982).
3. Department of Chemical Engineering, Yale University, New Haven, CT (July 1982).
5. AFOSR/AFRPL Rocket Propulsion Research Meeting, Lancaster, CA (March 1983).
11. IBM Research Laboratory, San Jose, CA (May 1984).
The October 1982 invitation to I.I.T. was further used to visit with Dr. A. Snelson of the I.I.T. Research Institute to discuss his work on identification of metal oxychloride species and their earlier work on ignition of doped light metal powders. Several telephone discussions with Dr. Michael Slack of the Grumman Co. took place that year to obtain his input on the status of the rocket combustion aspects of boron containing fuels. In March 1983, Dr. Fontijn spent a day at the Air Force Rocket Propulsion Laboratory, to discuss joint research interests with Dr. D.P. Weaver and his group. At the invitation of Dr. Weaver he reviewed the status of "The Use of Laser-Induced Fluorescence for Fundamental Kinetic Measurements", at the above-mentioned AIAA Thermophysics Conference. In November 1983 we held several meetings with Drs. J. Tishkoff and G.M. Faeth of AFOSR, first at RPI and then in Providence during the Eastern Section Meeting of the Combustion Institute. The purpose of those meetings was to review the status of boron combustion, particularly with regard to air-breathing rockets. Several recommendations for additional efforts by other investigators resulted from these discussions, which were extended during the June 1984 AFOSR specialists meeting on boron combustion.

At several of the above conferences in-depth discussions with the above and other Air Force and contractor personnel took place. Among the latter
Dr. M.K. King of Atlantic Research Co. should be mentioned. Dr. Kizirnis of AFWL Wright-Patterson Air Force Base contacted us to obtain information on the status of boron combustion diagnostics.

V. REFERENCES


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