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COMBUSTION KINETICS OF METAL OXIDE AND HALIDE RADICALS
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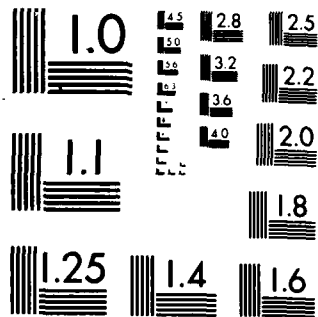
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To help provide a better understanding of the temperature dependence of the kinetics of diatomic metal radical oxidation reactions, experimental measurements have been made in the 450 to 1750 K temperature regime. An HTFFR (high-temperature fast-flow reactor) has been used. The metal radical concentrations were measured by laser-induced fluorescence. The general uses of this spectro-metric 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 AgO , AgCl and BCl . Production methods for these are discussed. For the reaction

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$\text{Al}_2\text{O} + \text{CO}_2 + \text{Al}_2\text{O}_2 + \text{CO}$ 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 $D(\text{O-Al}_2\text{O}) > D(\text{O-CO}) = 530 \text{ kJ mol}^{-1}$, which

is in apparent disagreement with the OAl_2O dissociation energy obtained for Al_2O_2 from Al_2O_3 evaporation-mass spectrometry studies. It is argued that the latter

Al_2O_2 may have a different structure from that of the present work. For the

reaction between AlCl_2 and 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 $\text{Al}_2\text{O}_2 + \text{Cl}$ product channel dominates at lower temperatures, while

the $\text{OAlCl}_2 + \text{O}$ channel dominates at higher temperatures. The $\ln k(T)$ versus $1/T$ dependence of the AlCl_2/O_2 reaction is contrasted to those observed for the

AlO/O_2 and BF/O_2 reactions. Quantitative results on BCl_2 have not yet been obtained due to a reaction between this radical and the Al_2O_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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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.¹ 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:
 - $\text{BCl} + \text{O}_2 \longrightarrow$ Emissions from Air Breathing Missile Plume After Burning
 - $\text{AlO} + \text{CO}_2 \longrightarrow$ Combustion of Aluminized Composite Propellants
 - $\text{BO} + \text{O}_2 \longrightarrow$ Combustion of Boron Slurries
 - $\text{AlCl} + \text{O}_2 \longrightarrow$ Microparticulates Formation
 - $\text{AlF} + \text{O}_2 \longrightarrow$ Tendency of Fluorinated Binders to Reduce Agglomeration
- OBTAIN THESE $k(T)$ DATA OVER THE 300–2,000 K RANGE. NON-ARRHENIUS BEHAVIOR PRECLUDES EXTRAPOLATION FROM NARROW TEMPERATURE INTERVALS.

TECHNIQUE

High-Temperature Fast-Flow Reactor

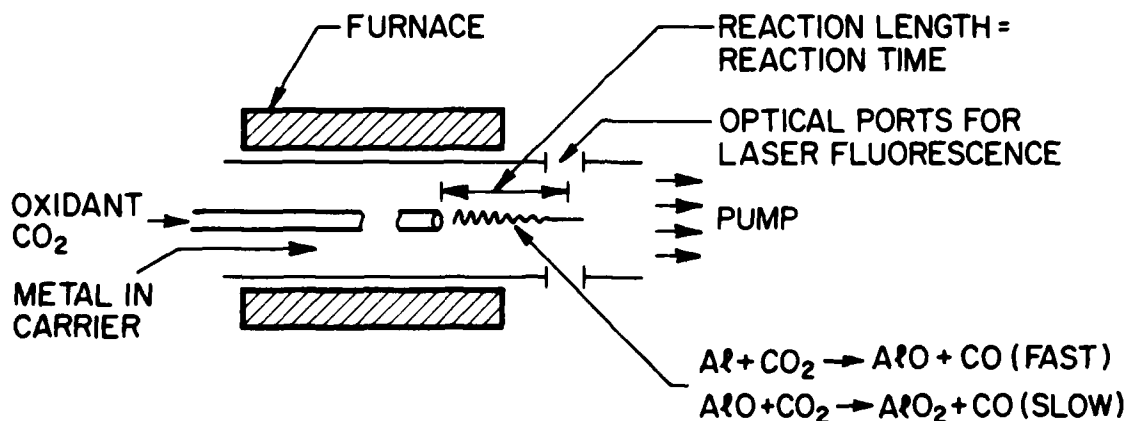


Fig. 1

II. RESULTS

A. Cumulative Chronological List of Publications and Their Abstracts

1. A. Fontijn and M.A.A. Clyne, Eds., Reactions of Small Transient Species,* Kinetics and Energetics, Academic Press, London, 1983.
2. A. Fontijn and R. Zellner, "Influence of Temperature on Rate Coefficients of Bimolecular Reactions," in *ibid.*, Chap. 1.*
3. A. Fontijn, "Use of Laser-Induced Fluorescence for Fundamental Gas-Phase Kinetic Measurements," *Progress in Astronautics and Aeronautics*, 92, 147-174 (1984).

The uses of laser-induced fluorescence (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 O 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.

4. A. Fontijn, "Combustion Kinetics of Metal Atoms and Metallic Radicals Over Wide Temperature Ranges," 21st JANNAF Combustion Meeting, CPIA Publication 421, Vol. 1, 45-52 (October 1984).

The dependence of the rate coefficients of gas-phase oxidation reactions of metallic species on temperature is discussed. Examples given pertain primarily to A₂ and B species reactions in the 300 - 1900 K range. These reactions show a wide variety of $\ln k(T)$ 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

5. D.F. Rogowski, A.J. English and A. Fontijn, "An HTFFR Kinetics Study of the Reaction $\text{AlO} + \text{CO}_2 \rightarrow \text{AlO}_2 + \text{CO}$. Thermochemical Implications," Journal of Physical Chemistry, in press.

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 $[\text{AlO}]$. $k(T)$ was determined to be $(2.5 \pm 1.3) \times 10^{-14} \exp [(400 \pm 280)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (confidence level > 95%). The reaction probably proceeds via an intermediate complex which preferentially dissociates to the reactants. The negative activation energy implies $D(\text{O-AlO}) > D(\text{O-CO}) = 530 \text{ kJ mol}^{-1}$, which is incompatible with the O-AlO dissociation energy obtained for AlO_2 from Al_2O_3 evaporation-mass spectrometry studies. It is argued that the latter AlO_2 may have a different structure from that of the present work.

6. A. Fontijn, "Temperature Dependence of the Kinetics of Elementary Combustion Reactions of Refractory Species," Combustion Science and Technology, in press.

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 Al and B species reactions in the 300 - 1900 K range. These reactions show a wide variety of $\ln k(T)$ 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.

7. D.F. Rogowski and A. Fontijn, "An HTFFR Kinetics Study of the Reaction Between AlCl and O_2 from 490 to 1750 K," 21st Symposium (International) on Combustion, submitted.*

A method for the production of 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 $\text{AlO}_2 + \text{C}_2$ product channel dominates at lower temperatures, while the $\text{OAlC}_2 + \text{O}$ channel dominates at higher temperatures. The $\ln k(T)$ versus T^{-1} dependence of the AlC_2/O_2 reaction is contrasted to those observed for the AlO/O_2 and BF/O_2 reactions.

B. Some Illustrative Discussion

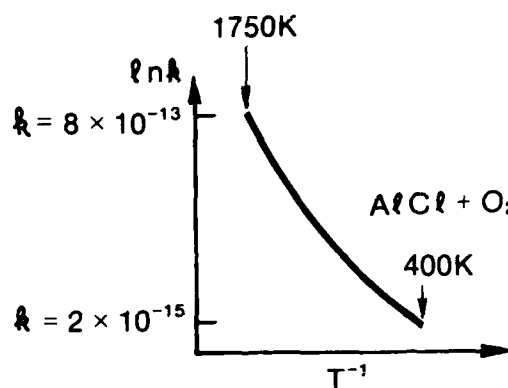
Some of the results from the publications given above are illustrated in Fig. 2. The AlC_2/O_2 reaction has a $\ln k$ versus T^{-1} plot with gradual curvature, somewhat similar to that observed in many reactions between hydrocarbon molecules and OH radicals, but different from any plot observed in previous 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 OAlC_2 and AlO_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, AlO/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 Al/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 Al, by an electron

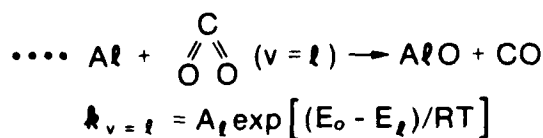
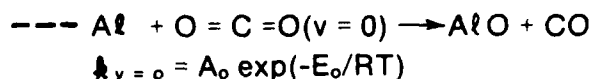
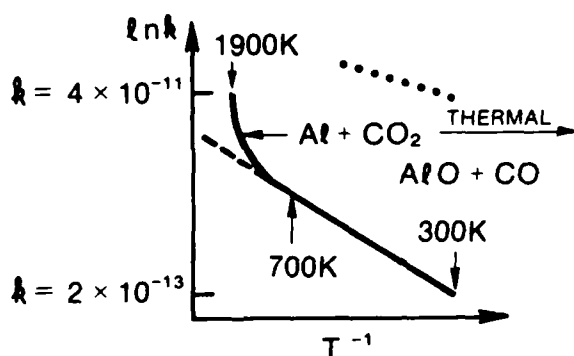
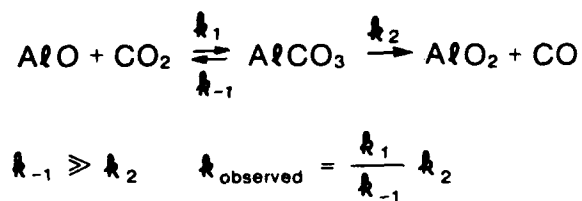
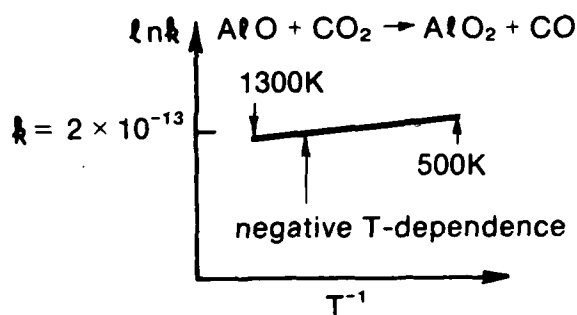
ACCOMPLISHMENTS

OBSERVATION

INTERPRETATION



$\text{OAlCl} + \text{O}$
DOMINATES AT HIGH TEMPERATURES
 $\text{AlO}_2 + \text{Cl}$
DOMINATES AT LOW TEMPERATURES



k in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

$A_l \gg A_0$, i.e. BENT CO_2
HAS MUCH LARGER REACTION
CROSS SECTION THAN LINEAR CO_2

Fig. 2

jump ionic mechanism which interaction takes place at larger internuclear distances (and hence reaction cross sections) than the covalent interaction of ground state CO_2 . The absence of a similar dependence on the vibrational excitation of CO_2 in the AlO/CO_2 reaction can be attributed to the larger ionization potential I.P. of AlO (I.P. = 9.5 ± 0.5 eV) compared to Al (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 reactions. Many more reactions need studying to arrive at a meaningful predictive ability.

C. Boron Species Observations

Considerable effort has been spent to produce BCl and study its reactions. 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 BCl production.

According to Krenev *et al*⁷ BCl can be produced in a flow tube by passing BCl_3 over solid boron in the 1373 to 1573 K temperature regime. By flowing BCl_3/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) transition of BCl . However, similar signals were observed when the boron was removed. Thus the signals observed can largely be attributed to BCl_3 dissociation. Since this process would continue in the reaction zone, a method for BCl production involving BCl_3 is unsuitable for HTFFR kinetics observations. We next produced BCl by passing Cl_2 over B chunks at 1100 to 1200 K, which also gave strong BCl signals. This method was used for studies of $\text{BCl} + \text{O}_2$ 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 BCl 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 BCl/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 BCl/O_2 reaction kinetics. An investigation of the cause of this apparatus effect showed that (i) BCl signals were produced when a reaction tube had been used for a while and the B chunks and Cl_2 were removed, (ii) with B chunks and Cl_2 present, but no added Al, strong LIF signals of $AlCl$ were observed and (iii) with a new reaction tube very strong BCl 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_2O_3/SiO_2 (McDanel MV 30) reaction tube walls and replace Al. Similar problems were not encountered when next we produced $AlCl$ by passing Cl_2 over an Al wetted tungsten coil: kinetic studies of the $AlCl + O_2$ reaction yielded rate coefficients independent of the reaction tube distance and flow velocity used.⁴

It still appears possible to study BCl reactions with reaction tubes made of other wall materials or coated with a suitable compound. A quartz tube appears to be one possibility,¹¹ 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 BC₂ 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).
4. Department of Chemistry, Illinois Institute of Technology, Chicago, IL (October 1982).
5. AFOSR/AFRPL Rocket Propulsion Research Meeting, Lancaster, CA (March 1983).
6. United Technologies Research Center, East Hartford, CT (April 1983).
7. AIAA 18th Thermophysics Conference, Montreal, P.Q., Canada (May 1983).
8. Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY (February 1984).
9. AFOSR/AFRPL Rocket Propulsion Research Meeting, Lancaster, CA (March 1984).
10. Department of Chemistry, Louisiana State University, Baton Rouge, LA (March 1984).
11. IBM Research Laboratory, San Jose, CA (May 1984).
12. AFOSR Specialists Meeting on Boron Combustion, Pittsburgh, PA (June 1984).

13. 21st JANNAF Combustion Meeting, Laurel, MD (October 1984).
14. Eastern Section, The Combustion Institute, Clearwater Beach, FL (December 1984).
15. Bell Aerospace Textron Co., Buffalo, NY, (March 1985).
16. Department of Chemical Engineering, State University of New York, Buffalo, NY (March 1985).
17. Department of Chemistry, York University, Toronto, Ont., Canada (March 1985).
18. Department of Chemistry, University of New South Wales, Sydney, N.S.W., Australia (June 1985).
19. Eastern Section, The Combustion Institute, Philadelphia, PA (November 1985).
20. AT&T Bell Laboratories, Murray Hill, NJ (November 1985).
21. Amoco Research and Development Center, Naperville, IL (November 1985).

The October 1982 invitation to I.I.T. was further used to visit with Dr. A. Snelson of the I.T.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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2. A. Fontijn and W. Felder, "High Temperature Flow Tubes. Generation and Measurement of Refractory Species," Reactive Intermediate in the Gas Phase. Generation and Monitoring, D.W. Setser, Ed., (Academic Press, New York, 1979), Chap. 2.
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4. D.F. Rogowski and A. Fontijn, "An HTFFR Kinetics Study of the Reaction Between AlCl_3 and O_2 From 490 to 1750 K," Twenty-first Symposium (International) on Combustion, submitted.
5. D.F. Rogowski, A.J. English and A. Fontijn, "An HTFFR Kinetics Study of the Reaction $\text{Al}_2\text{O} + \text{CO}_2 \rightarrow \text{Al}_2\text{O}_2 + \text{CO}$. Thermochemical Implications," J. Phys. Chem., in press.
6. A. Fontijn and W. Felder, "HTFFR Kinetics Studied of $\text{Al} + \text{CO}_2 \rightarrow \text{AlO} + \text{CO}$ from 300 to 1900 K, a Non-Arrhenius Reaction," J. Chem. Phys. **67**, 1561 (1977).
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