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COMBUSTION KINETICS OF METAL OXIDE AND HALIDE RADICALS

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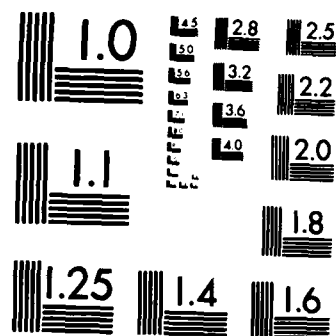
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Current ability to influence combustion involving metals is severely hampered by a lack of understanding and knowledge of the ways and manner by which temperature affects the rate coefficients of individual reactions and reaction channels. The commonly-used Arrhenius equation predicts a logarithmic dependence of rate coefficients on inverse temperature. This is often not the case and order of magnitude errors can result in extrapolations based on this equation. This report discussed various types of deviations from the equation observed in high-temperature fast-flow reactors. Laser-induced fluorescence measurements are used in such reactors to provide data necessary for obtaining an understanding of the oxidation reactions of boron and aluminum-containing radicals, as a function of temperature.					
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TABLE OF CONTENTS

	Page
I. RESEARCH OBJECTIVES	1
II. STATUS OF THE RESEARCH EFFORT	3
III. CUMULATIVE LIST OF PUBLICATIONS	6
IV. PROFESSIONAL PERSONNEL	7
V. PRESENTATIONS AND OTHER INTERACTIONS	7
VI. REFERENCES	9

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I. RESEARCH OBJECTIVES

Current ability to improve the efficiency of metal combustion is severely hampered by a lack of understanding and knowledge of the ways and manner by which temperature affects the rate coefficients of individual reactions and reaction channels. While the simple Arrhenius-type equation $k(T) = AT^{1/2} \exp(-E_A/RT)$ 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 equation¹. It is the goal of the present program to provide an insight in the kinetic behavior of metallic radical oxidation reactions as influenced by temperature.

Figure 1 shows the reactions which we plan to study and their relevance to advanced propulsion systems development. It also gives a schematic of the HTFFR, high-temperature fast-flow reactor, method we are using to generate the metallic radicals and measure their oxidation kinetics. This unique tool 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 our work with this apparatus are to be:

- (i) A $k(T)$ expression for the 300 - 2000 K temperature range for each of a number of metallic radical oxidation reactions.
- (ii) Based on (i), an improved understanding of the chemistry which governs the temperature dependence of such reactions.

HIGH TEMPERATURE COMBUSTION KINETICS OF METALS

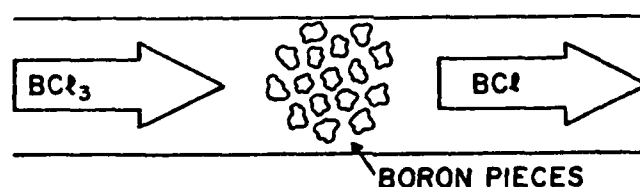
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GOALS

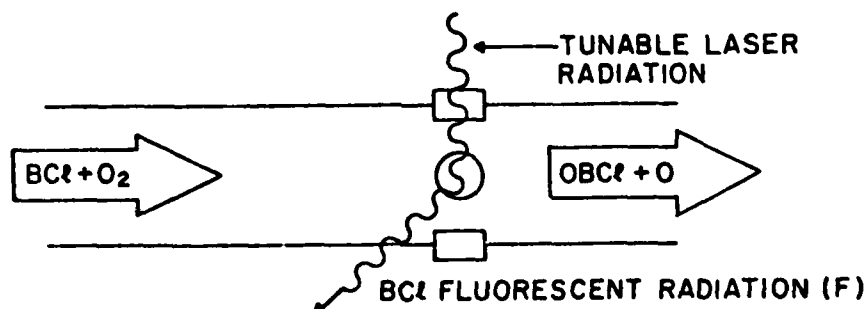
- UNDERSTAND THE MECHANISMS OF METALLIC RADICAL OXIDATION REACTIONS.
- MEASURE REACTION RATE COEFFICIENTS FOR REACTIONS IMPORTANT TO ADVANCED PROPULSION SYSTEMS:
 - $\text{BCl} + \text{O}_2 \rightarrow$ Emissions from Air Breathing Missile Plume After Burning
 - $\text{AlO} + \text{CO}_2 \rightarrow$ Combustion of Aluminized Composite Propellants
 - $\text{BO} + \text{O}_2 \rightarrow$ Combustion of Boron Slurries
 - $\text{AlCl} + \text{O}_2 \rightarrow$ Microparticulates Formation
 - $\text{AlF} + \text{O}_2 \rightarrow$ 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

1. PRODUCE REACTANT IN HIGH TEMPERATURE FLOW TUBE



2. REACT WITH OXYGEN IN VARIABLE TEMPERATURE FLOW TUBE



$$\ln \frac{F_{1+0}}{F_1} = k(T)[\text{O}_2]t$$

Figure 1

II. STATUS OF THE RESEARCH EFFORT

Figure 2 illustrates the type of results and understanding which results from HTFFR work. A more detailed discussion of current insight into Arrhenius and non-Arrhenius behavior is given in Ref.1. While it should be clear from that discussion that we have not yet reached the point that behavior can readily be predicted, it is also evident that far more is known for combustion reactions of hydrocarbons than for those of metallic radicals. Data for metallic radical oxidation reactions are needed. In addition to the direct use such data would have in advanced propulsion system design work, they would form the basis for an understanding of this class of reactions. The understanding would in turn allow meaningful extrapolations from known reactions to further similar reactions of interest.

The reaction



is $\approx 25 \text{ kJ mol}^{-1}$ endothermic and follows the Arrhenius equation quite well². Both the presence of an inherent energy barrier, due to the endothermicity, and the similarity in geometry of the SO_2 and SO_2^- molecules (compare reaction (3) below), favor such "normal" behavior¹.

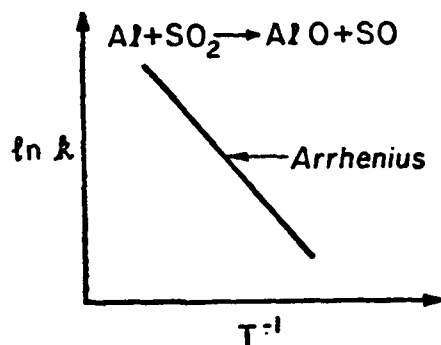
The slight negative temperature dependence (i.e., decrease in k with increasing temperature) observed³ for



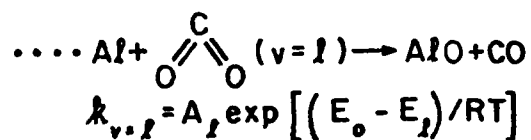
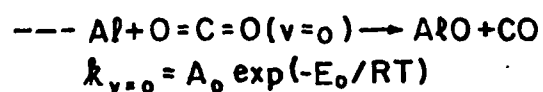
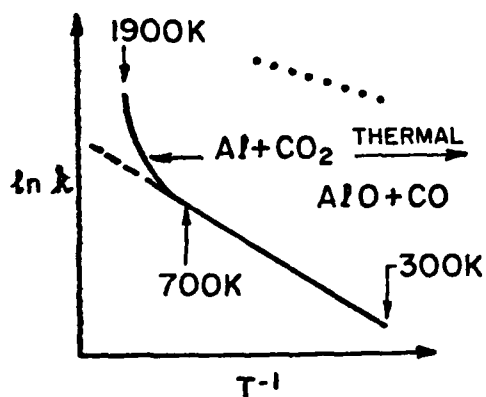
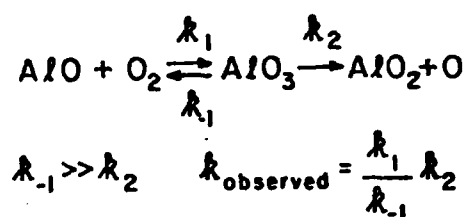
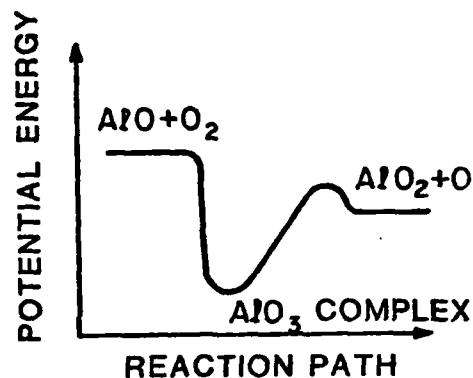
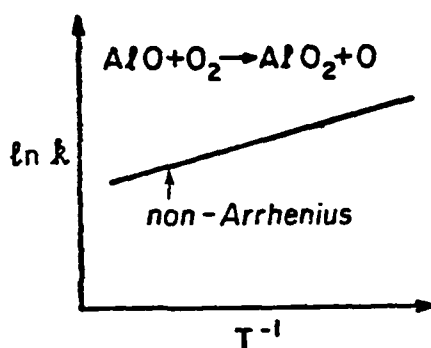
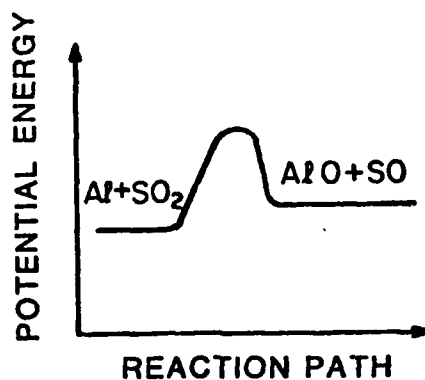
was most unexpected; it may be attributed to formation of an intermediate bound complex, which preferentially dissociates to the reactants rather than the products¹. This reaction is the only metallic radical oxidation reaction for which $k(T)$ data have been

ACCOMPLISHMENTS

OBSERVATION



INTERPRETATION



$A_1 \gg A_0$, i.e. BENT CO_2
HAS MUCH LARGER REACTION
CROSS SECTION THAN LINEAR CO_2

Figure 2

obtained. However, we have also obtained room temperature data for the reaction⁴



which at that temperature is nearly an order of magnitude faster than the AlO/O_2 reaction. Both reactions are likely to proceed by covalent rather than ionic mechanisms and the larger k_3 (300 K) indicates a higher Arrhenius A factor, suggesting that either no intermediate bound complex is formed or at least that it does not dissociate preferentially to the reactants⁴. Thus, for reaction (3) we predict a more positive temperature dependence than for reaction (2), which we will attempt to verify experimentally.

The most interesting, and least anticipated, result obtained⁵ thus far is that for the reaction



The very rapid increase in k_4 above 700 K can be attributed to the thermal equilibrium increase in the concentration of CO_2 in bending vibrational modes. Contrary to ground-state linear CO_2 , which has a negative electron affinity and can only interact with Al by a covalent mechanism, bent CO_2 can interact at larger distances by an ionic (electron jump) mechanism^{1,5}.

Due to the presence of the electronegative O atom in AlO a predominant ionic mechanism for



is unlikely. Hence an a priori prediction for reaction (5) is that its kinetic behavior will be quite different from reaction (4). Quite possibly it will show a slight concave upward curvature of the Arrhenius plot, as observed in several hydrocarbon oxidation reactions¹. We have

commenced a study of reaction (5). While we had originally planned to first study the $\text{BCl} + \text{O}_2$ reaction, illustrated in Figure 1, we now anticipate to study that reaction next. This approach is likely to lead to faster results, as discussed below.

The design and operation of the HTFFR constructed under this grant have been described in the preceding progress report⁶. Basically, it consists of two vertical high temperature reactors in series. In the upstream reactor the metallic radical is produced. In the downstream reactor the relative concentration of these radicals is measured by laser-induced fluorescence as a function of $[\text{O}_2]$, P, T and t to determine $k(T)$. The sensitivity of the fluorescence technique⁷ allows observation on very low radical concentrations ($10^9 - 10^{11} \text{ cm}^{-3}$), which prevents interference from nucleation reactions. The major portion of our experimental efforts this year has been spent on completion and testing of the facility. These preliminary experiments suggested that it would be advisable to have the operators gain experience with the new facility gradually. Since we have considerable experience with Al reactions, and the BCl production method is novel, we therefore decided, in consultation with the technical monitor, to study reaction (5) first.

III. CUMULATIVE LIST OF PUBLICATIONS

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*, accepted for publication.

IV. PROFESSIONAL PERSONNEL

Mr. Andrew J. English, like last year, has spent his research time on the present work. The results of our efforts to date are collected in his Master of Engineering thesis of December 1983, entitled: "High-Temperature Fast-Flow Reactor for the Study of Metallic Radical Combustion Reactions."

In the early part of the year we were assisted by Dr. Sergio L.P. Monteiro and later on by Jeff Hyatt and Robert Crocker, undergraduate research assistants.

V. PRESENTATIONS AND OTHER INTERACTIONS

In the past year, Dr. Fontijn presented papers and seminars related to high temperature reactions of metallic species at the:

1. AFOSR/AFRPL Rocket Propulsion Research Meeting, Lancaster, CA (March 1982).
2. United Technologies Research Center, East Hartford, CT (April 1983).
3. AIAA 18th Thermophysics Conference, Montreal, P.Q., Canada (May 1983).

In March, 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 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 these meetings was to review the status of boron combustion, particularly with regard to air-breathing rockets. Several recommendations for additional efforts resulted from these discussions, particularly:

- (i) That a basic experimental study be made of the processes occurring at and near the surface of boron particles during combustion. The importance of this is suggested by the recent work of Glassman et al.⁸.
- (ii) That experiments be made on the combustion of boron slurries, where the regular hydrocarbons are replaced in part with partially chlorinated hydrocarbons. The presence of chlorine (or other halogens) could result in increased evaporation of the combustion-inhibiting oxide film on the surface of the boron particles. Several pieces of information point in this direction, e.g., Refs.9,10.
- (iii) Since agglomeration of boron particles in the gas phase appears to be a problem, the use of additives to inhibit this process should be considered. Such an approach would be similar to the use of additives in soot-inhibition^{11,12}.
- (iv) That a workshop on the subject, for which adequate basic information is lacking, be held in 1984. In December, we sent Dr. Tishkoff a list of some potential participants, who are knowledgeable in various aspects of boron oxidation.

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1. A. Fontijn and R. Zellner, "Influence of Temperature on Rate Coefficients of Bimolecular Reactions," Reactions of Small Transient Species. Kinetics and Energetics, A. Fontijn and M.A.A. Clyne, Eds. (Academic Press, London, 1983), Chap.1.
2. A. Fontijn and W. Felder, "HTFFR Kinetics Studies of the Al/SO_2 Reaction from 700 - 1600 K. Implications for $D(Al-O)$," J. Chem. Phys. 71, 4854 (1979).
3. A. Fontijn, W. Felder and J.J. Houghton, "HTFFR Kinetics Studies. Temperature Dependence of Al/O_2 and AlO/O_2 Kinetics from 300 to 1700/1400 K," Sixteenth Symposium (International) on Combustion, (The Combustion Institute, Pittsburgh, 1977), p.871.
4. I.P. Llewellyn, A. Fontijn and M.A.A. Clyne, "Kinetics of the Reaction $BO + O_2 \rightarrow BO_2 + O$," Chem. Phys. Lett. 84, 504 (1981).
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