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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Advanced propulsion system designs require quantitative understanding of the temperature-dependent kinetics of the gas-phase oxidation reactions of the metallic fuel components. To this end experimental rate coefficient measurements have been made on aluminum and boron species, in the 440-1830 K temperature range, in a high-temperature fast-flow reactor (HTFFR). Results are reported for the following individual reactions: Al + N ₂ O; AlO + Cl ₂ ; AlO + HCl; AlO + CH ₄ ; AlCl + CO ₂ ; AlCl + N ₂ O; AlCl + HCl; BCl + CO ₂ ; BCl + N ₂ O; BCl + SO ₂ . The reaction products are discussed. For several series of homologous exothermic reactions correlations are established between the activation barriers and the sums of the s-p (or sigma-pi) promotion energies and the ionization potentials of the metallic reactants minus the electron affinities of the oxidants. These series are the reactions of alkali metal atoms with N ₂ O, group 2 and transition metal atoms with N ₂ O, boron group atoms with N ₂ O, and AlCl, BCl, BF and BH with O ₂ , CO ₂ , N ₂ O and SO ₂ . These correlations are explained on the basis of chemical resonance theory. Calculations based on this semi-empirical approach are shown to agree well with experiment.			
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TABLE OF CONTENTS

	<u>Page</u>
I. RESEARCH OBJECTIVES	1
II. RESULTS	2
A. CUMULATIVE CHRONOLOGICAL LIST OF PUBLICATIONS	2
B. SOME AMPLIFICATION	6
III. PROFESSIONAL PERSONNEL	10
IV. PRESENTATIONS AND OTHER INTERACTIONS	11
REFERENCES	13

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I. RESEARCH OBJECTIVES

Current ability to transfer engineering data, on rocket chamber and plume combustion, from present to advanced propulsion systems, is hampered by a lack of understanding and knowledge of individual A1 and B species reactions and the ways by which temperature affects the reaction rate coefficients. The Arrhenius equation $k(T) = A \exp(-E/RT)$ has over limited temperature ranges been of great value. However, over the large temperature ranges of interest to rocket propulsion systems, order of magnitude errors can be made by extrapolations based on it, particularly for exothermic and slightly endothermic reactions.¹ Other $k(T)$ expressions and current theory are inadequate to predict or describe the observations made thus far for reactions of metallic propellant species.

A major goal of the work has been to provide, through accurate measurements, reliable data on, and improved insight into, the kinetic behavior of A1 and B atom, halide and oxide radical oxidation reactions, as influenced by temperature. The measurements have been made using the HTFFR (high-temperature fast-flow reactor) technique. HTFFRs are unique tools, which 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 1900 K to provide wide range $k(T)$ (temperature-dependent rate coefficient) data. In the work reported, laser-induced fluorescence, LIF, has been used to monitor the metallic radical reactant concentrations, as a function of time, concentration of the molecular oxidant (present in excess), temperature and pressure.

One of the reasons improved insight is a major goal of research is that it should allow the development of a predictive ability. Confirmation of predictions not only establishes the validity of the understanding obtained, but also allows an extension of the

data base available to modelers. Thus engineering design can become more reliable on a shorter timescale than when all data have to be obtained experimentally. One of the goals of the present work has been to use the data obtained to establish, and explain, correlations for a few series of homologous exothermic reactions.

These general objectives and a systematic of the experimental facility are illustrated in Fig. 1.

II. RESULTS

A. CUMULATIVE CHRONOLOGICAL LIST OF PUBLICATIONS

1. A.G. Slavejkov and A. Fontijn, "HTFFR Kinetics Studies of the Reactions of AlCl and BCl with HCl at High Temperatures", *Chemical Physics Letters*, **165**, 375-378 (1990).

The kinetics of the title reactions have been investigated in a high-temperature fast-flow reactor (HTFFR). The observed temperature dependences of the rate coefficients are described, in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, by the expressions: AlCl + HCl (1), $k_1(T) = 1.1 \times 10^{-11} \exp(-13100 \text{ K}/T)$ between 1330 and 1610 K, and BCl + HCl (2), $k_2(T) = 1.2 \times 10^{-10} \exp(-12100 \text{ K}/T)$ between 1250 and 1620 K. Confidence limits are given in the text.

2. A.G. Slavejkov, C.T. Stanton, and A. Fontijn, "High-Temperature Fast-Flow Reactor Kinetic Studies of the Reactions of AlO with Cl₂ and HCl Over Wide Temperature Ranges", *The Journal of Physical Chemistry*, **94**, 3347-3352 (1990).

The kinetics of the title reactions have been studied in a high-temperature fast-flow reactor (HTFFR). The relative concentrations of AlO were monitored by laser-induced fluorescence at the B²Σ-X²Σ and C²Σ-X²Σ transitions. The following k(T) expressions in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ are obtained: AlO + Cl₂ (1), $k_1(T) = 3.0 \times 10^{-10} \exp(-1250 \text{ K}/T)$ between 460 and 1160 K; AlO + HCl (2), $k_2(T) = 5.6 \times 10^{-11} \exp(-139 \text{ K}/T)$ between 440 and 1590 K. Confidence limits are given in the text. No fluorescence from a potential four-center product AlCl could be detected. From this it is estimated that less than 5% of the AlO reacted produced AlCl, which indicates that abstraction reactions dominate, i.e., OAlCl + Cl for reaction (1) and OAlCl + H and/or AlOH + Cl for reaction (2).

PROBLEM

- CURRENT MODELS OF AI AND B COMBUSTION IN ROCKET MOTORS AND EXHAUSTS LACK RELIABLE CHEMICAL KINETIC INPUT DATA, WHICH HAMPERS DEVELOPMENT OF ADVANCED SYSTEMS

GOALS

- OBTAIN KINETIC DATA OVER THE 300-1900 K RANGE. CHANGING MECHANISMS AND NON-ARRHENIUS BEHAVIOR PRECLUDE EXTRAPOLATION FROM NARROW TEMPERATURE INTERVALS
- ESTABLISH AND UNDERSTAND THE KINETICS OF AI AND B SPECIES COMBUSTION REACTIONS NEEDED FOR PROPULSION SYSTEM MODELS.
- FIND, AND INTERPRET THEORETICALLY, CORRELATIONS BETWEEN KINETIC PARAMETERS WITHIN HOMOLOGOUS SERIES OF REACTIONS, IN ORDER TO MAKE PREDICTIONS FOR FURTHER REACTIONS

TECHNIQUE USED

- HIGH-TEMPERATURE FAST-FLOW REACTOR WITH LASER-INDUCED FLUORESCENCE

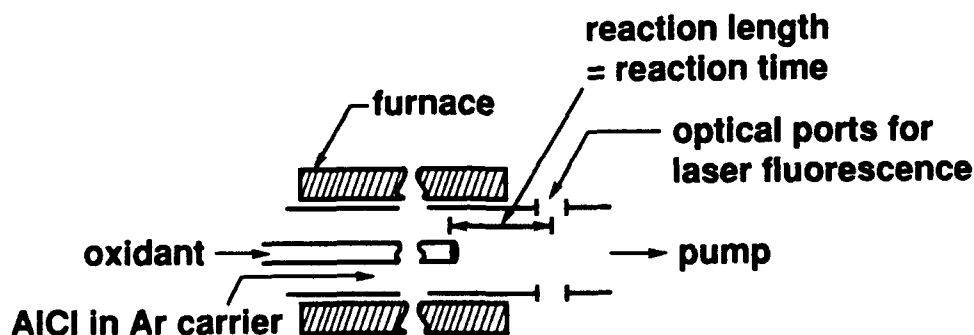


Figure 1. Problem, goals and technique.

3. A.G. Slavejkov, P.M. Futerko, and A. Fontijn, "High-Temperature Fast-Flow Reactor Kinetics Study of the Reaction Between BCl and CO₂ From 770 to 1830 K", Twenty-Third Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1990, pp. 155-161.

The kinetics of the title reaction have been studied under pseudo-first order conditions in a high-temperature fast-flow reactor (HTFFR). BCl radicals were generated by a two-stage method that combines microwave discharge with thermal dissociation of BCl₃. The Arrhenius plot has pronounced curvature over the temperature range investigated. The best three-parameter fit to the measured rate coefficients yields $k(T) = 1.8 \times 10^{-31} (T/K)^{5.6} \exp(-1180 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with 2σ precision limits of $\pm 20\%$ and 2σ confidence limits of $\pm 30\%$. These $k(T)$ are compared to those for the reactions of BCl with O₂ and AlCl with O₂ and CO₂. Arguments are advanced that suggest that all these reactions may proceed by O-atom abstraction leading to oxychloride formation. An explanation for the larger rate coefficients of the BCl as compared to the corresponding AlCl reactions is given.

4. P.M. Futerko and A. Fontijn, "Activation Barriers for Series of Exothermic Homologous Reactions. I. Metal Atom Reactions with N₂O", The Journal of Chemical Physics, 195, 8065-8071 (1991).

We recently observed that the activation barriers of O-atom abstraction reactions between metal atoms and N₂O, in which both reactants are in their ground electronic states and the atoms contain no valence *p* electrons, vary systematically with the sums of the metal atom ionization potential and the energy required to promote a valence *s* electron to the lowest *p* orbital. It is shown here that this observation can be explained by the assumption that the activated complex results from the resonance interactions of ionic and covalent structures. Activation barriers for 43 reactions are calculated and where experimental measurements are available, are shown to be in good agreement with those. New interpretations are offered for literature data on the Ca and Cr reactions. The resonance treatment leads to a more general relationship in which activation barriers depend simultaneously on ionization potentials, electron affinities, promotion energies, and bond energies of the reactants. A number of further series of reactions, where activation barrier or rate coefficient trends with some of these parameters have been observed, are discussed and seen to be special cases of this formalism. Good agreement is found between the height of the barrier for the N₂O + H → N₂ + OH reaction calculated by the present resonance treatment and an *ab initio* method.

5. A. Fontijn and P.M. Futerko, "Homogeneous Kinetics of Metal Species over Wide Temperature Ranges: Techniques, Measurements, and Correlations", Gas-Phase Metal Reactions, A. Fontijn, Ed., Elsevier, Amsterdam, in press, 28 pages.

The HTFFR (high-temperature fast-flow reactor) and Metals-HTP (high-temperature photochemistry) techniques for measurements of the kinetics of metallic species in the 300 to 1900 K temperature range are described. Their relative advantages and disadvantages are discussed. The most extensive data set obtained by the HTFFR

technique concerns the oxidation reactions of Al, AlO and AlCl. The various temperature dependences observed for these are summarized and discussed. The pre-exponentials of the rate coefficients of several of these reactions are compared to each other and to those obtained from HTFFR measurements on BCl oxidation reactions. HTP results for the Na/O₂/N₂ and Cr/O₂/Ar systems, as well as the Cu + N₂O reaction, are given. It is shown that for various groups of metal atom + N₂O reactions and for reactions of AlCl, BCl, BF and BH with various oxygen oxidants, the activation barriers correlate well with the ionization potentials plus the s-p (or σ-π) promotion energies of the metal species minus the electron affinities of the oxidants. These correlations can be explained on the basis of resonance theory and together constitute a generalization of more limited correlations for activation energies, already in common use. Semi-empirical calculations of the barrier energies based on the present approach are shown to agree well with experiment.

6. P.M. Futerko, A.G. Slavejkov, and A. Fontijn, "High-Temperature Fast-Flow Reactor Kinetics Studies of the Reactions of BCl with SO₂ and N₂O over Wide Temperature Ranges", The Journal of Physical Chemistry, to be submitted.

The kinetics of the title reactions have been studied in a high-temperature fast-flow reactor (HTFFR). The Arrhenius plot of the BCl + SO₂ reaction shows pronounced curvature over the 470 to 1690 K temperature range. The measured rate coefficients are best described by the three-parameter expression $k(T) = 7.8 \times 10^{-22} (T/K)^{3.0} \exp(-1680 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate coefficients of the BCl + N₂O reaction, obtained over the 660 to 1000 K temperature range, appear to exhibit normal Arrhenius behavior. The expression $k(T) = 3.0 \times 10^{-12} \exp(-5860 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been obtained from a best fit to the experimental data. Confidence limits are given in the text. The rate coefficients and activation barriers of these reactions, along with those of the BCl + O₂ and CO₂ reactions, have been found to correlate with the electron affinities of the oxidants.

7. P.M. Futerko and A. Fontijn, "Activation Barriers for Series of Exothermic Homologous Reactions. II. Comparison of Measurements to Theory for AlCl and BCl Reactions with Oxygen Oxidants", The Journal of Chemical Physics, to be submitted.

The kinetics of the reactions of AlCl with CO₂ and N₂O have been studied in a high-temperature fast-flow reactor (HTFFR). A least-squares fit of the rate coefficient measurements of the AlCl + CO₂ reactions has yielded $k(T) = 1.3 \times 10^{-19} (T/K)^{2.0} \exp(-4930 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 900 to 1790 K. The expression $k(T) = 1.2 \times 10^{-17} (T/K)^{2.0} \exp(-5830 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been obtained from a fit of the rate coefficient measurements of the AlCl + N₂O reaction over the 700 to 990 K temperature range. Confidence limits are given in the text. The height of the activation barriers of these reactions, along with those of several BCl, AlCl, BF and BH + reactions with further oxygen oxidants, have been found to correlate with the sum of the promotion energies and the ionization potentials of the Al and B species minus the electron affinities of the oxidants. A semi-empiric quantitative model to explain this relationship is presented.

8. P.M. Futerko, D.P. Belyung, and A. Fontijn, "Activation Barriers for Series of Exothermic Homologous Reactions. III. Comparison of Measurements to Theory for Reactions of Boron Group Atoms with Oxygen Oxidants", The Journal of Chemical Physics, to be submitted.

The kinetics of reactions between ground state Al atoms and N₂O has been studied in a high-temperature fast-flow reactor (HTFFR). The expression $k(T) = 2.2 \times 10^{-10} \exp(-1170 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been derived from a nonlinear regression analysis of the measured rate coefficient rate obtained over the 540 to 1020 K temperature range. Confidence limits are given in the text. The activation barriers for reactions between B, Al, Ga atoms and N₂O have been observed to correlate with the *s-p* promotion energies and ionization potentials of the metal atoms. An explanation is given for the correlation on the basis of chemical resonance theory, and a semi-empirical model of the activation barriers for reactions between these boron group atoms and N₂O, O₂, CO₂, SO₂ is derived. Activation barriers are calculated for the twelve reactions of this sequence.

9. D.P. Belyung and A. Fontijn, "Gas-Phase H-atom Abstraction from Hydrocarbons by Metal Oxides. The AlO + CH₄ Reaction from 590-1380 K", The Journal of Physical Chemistry, to be submitted.

Recent *ab initio* studies suggested that gaseous metal oxides could abstract H atoms from hydrocarbons, but with considerable barriers. To investigate this the title reaction has been studied from 590-1380 K in an HTFFR (*high-temperature fast-flow reactor*). The experiments yield $k(T) = 1.0 \times 10^{-10} \exp(-7481 \text{ K}/T) + 2.0 \times 10^{-13} \exp(-1978 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The activation energy indicated by the first term is in good agreement with the theoretical predictions, while the activation energy of the second term suggests a contribution of H-atom tunneling, leading to faster reaction at lower temperatures than indicated by the *ab initio* calculations.

B. SOME AMPLIFICATION

Our successfully attempts at correlations and their interpretation are described in publications 4, 5, 7, and 8 above. However, as numbers 7 and 8 are still in preparation, we give here a summary overview of what the status of our understanding in this respect is. We also briefly discuss number 9 further here.

In Fig. 2 results of some of our measurements on BCl + SO₂ reaction are shown. For such curved Arrhenius plots the term "activation energy" merely signifies the local slope of the plot at a given temperature. If we wish to compare the temperature dependence of reactions, a more useful approach is to use the expression

$$k(T) = AT^n \exp(-E/RT) \quad (1)$$

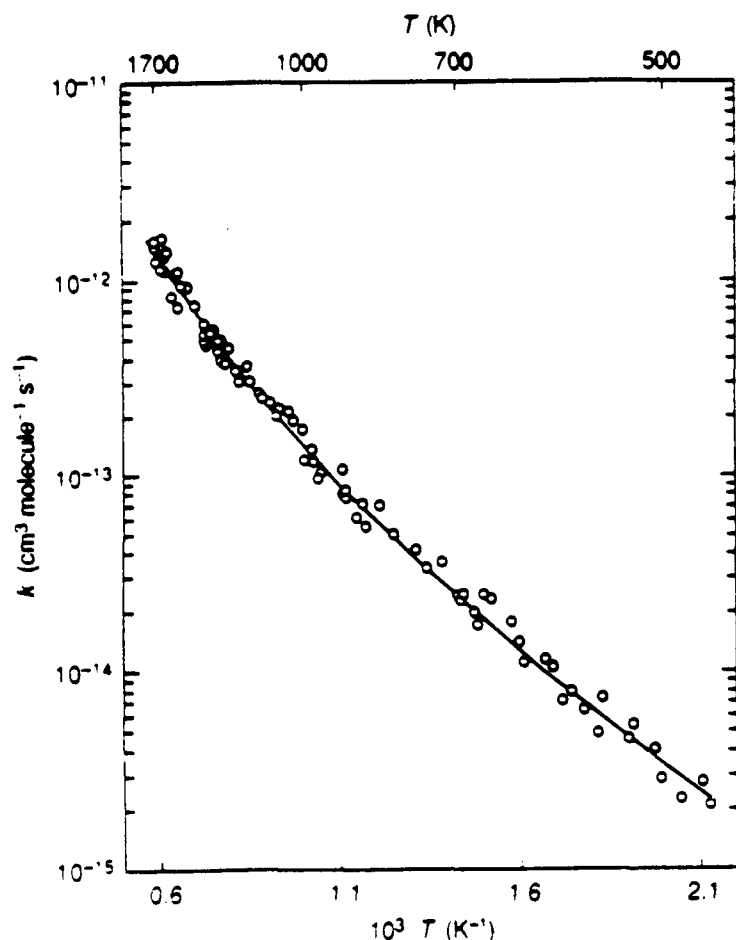


Figure 2. Arrhenius plot of the rate coefficient data of the $\text{BCl} + \text{SO}_2$ reaction from 460 to 1690 K. The solid line corresponds to the best-fit expression.

We have found for series of exothermic homologous reactions that by fixing n simple correlations exist between the "activation barriers" E and the sum of the σ - π , or s - p , promotion energies PE and the ionization potential IP of the metallic species minus the electron affinity EA of the oxidants. (In other words, we have extended the Evans-Polanyi relationships.) This is shown in Fig. 3 for a series of B and Al diatomic species reactions. In this case n has been taken to be 2.0, but values between 2 and 4 all give comparable correlations. Similarly, we get good agreement with this relationship for metal atom- N_2O reactions as shown in Fig. 4 (the EA term is left off here as only one oxidant is considered.) In this case n was taken as 0.5, but values between 0 and 1 give correlations nearly as good. Since n reflects the ratio of the

partition functions of the activated complex over those of the reactants, different groups of reactants should, of course, require different values of n .

These relationships can be understood in terms of resonance theory, as applied to the transition state. For example, consider the $\text{Mg} + \text{N}_2\text{O}$ reaction. In an *ab initio* study of the $1^1\text{A}'$ surface Yarkony² has determined that a large barrier inhibits the reaction. The height of this barrier is determined by the subtle interaction of single configuration wave functions Ψ_1 , Ψ_2 and Ψ_3 correlating asymptotically with $\text{Mg}(^1\text{S}) + \text{N}_2\text{O}(^1\Sigma^+)$, $\text{Mg}(^1\text{P}) + \text{N}_2\text{O}(^1\Sigma^+)$ and $\text{Mg}(^2\text{S}) + \text{N}_2\text{O}(^2\Pi)$. The wave function of the activated complex can be approximated by a superposition of these wave functions,

$$\Psi = c_1\Psi_1 + c_2\Psi_2 + c_3\Psi_3 \quad (2)$$

The energies of the corresponding configurations are determined by the physical properties given on the abscissae of Figs. 3 and 4. Most importantly for the metal atom- N_2O reactions the barrier height q for formation of the lowest-energy single configuration Ψ_1 should depend only on the $\text{N}_2\text{-O}$ bond energy according to Hirschfelder.³ The potential energy curves of the two excited configurations can be approximated, as functions of the metal atom-oxygen atom distance, by Morse curves where q replaces the bond energy parameter. The parameters which determine the shapes of the potential energy curves are obtained from an experimental activation barrier of one atom reaction of a group. For the remaining atoms the barriers are calculated by substituting the PE and IP of the respective metal atoms in the equations for the potential energy of the two excited configurations. For the three correlations in Fig. 4 we use parameters for the Morse curves from the experimentally measured N_2O reactions with Na, Cu, and Al, respectively. For each other oxidant the parameters can be determined by selecting one member of each group of reactions, which again allows predicting the others. These same parameters for each oxidant for the metal atom reactions have been used for the calculations on the diatomics shown in Fig. 3.

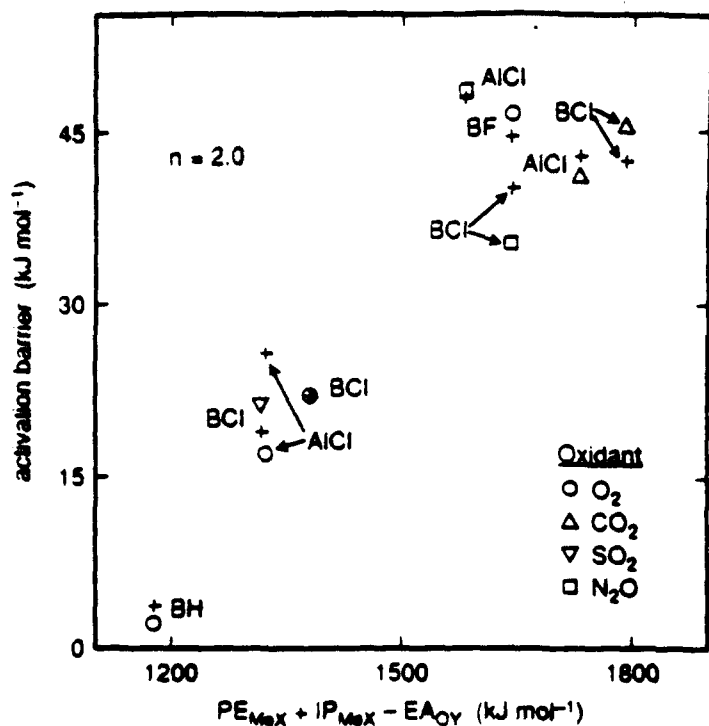


Figure 3. Plot of the experimental (open symbols) and calculated (plus signs) activation barriers of reactions between diatomic B and Al species, MeX , and oxygen species, OY , versus the sums of the σ - π promotion energy and ionization potentials of MeX minus the electron affinities of OY .

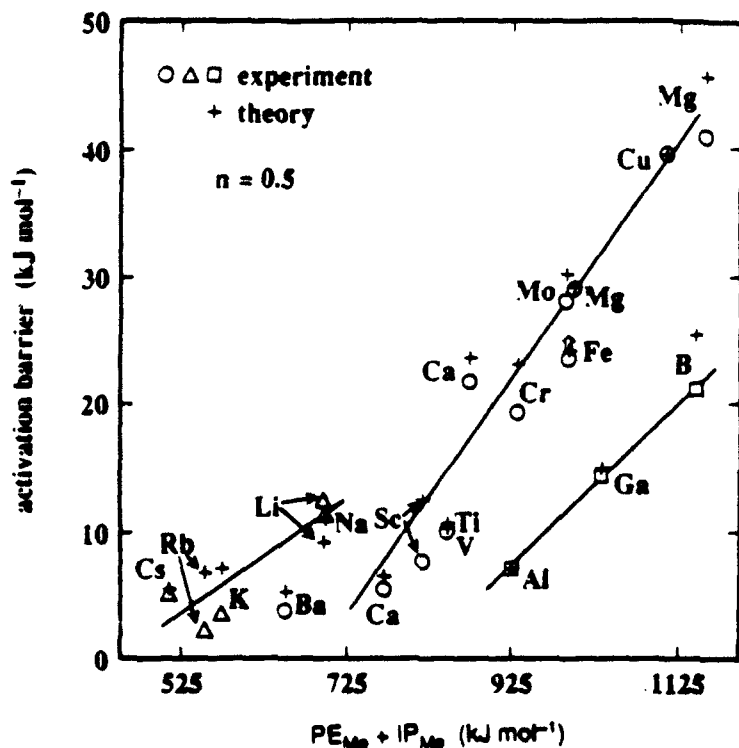


Figure 4. Plot of the experimental (open symbols) and calculated (plus signs) activation barriers for metal atom, Me , reactions with N_2O versus the sums of the s-p promotion energies and the ionization potentials of Me . The alkali metals (triangles) and boron group atoms (squares) are distinguished from the alkaline earth and transition metals (circles).

The reason that, in Fig. 4, the alkali metals fall on a different line from the group 2 and transition metals is the stronger resonance interactions in the former. This is caused by the presence of low-lying excited states and the resulting lengthening of the Me-O distance in the transition state.² The boron group metals also fall on a separate line. This is probably due to the p electrons in their ground states, which interact more strongly with the N₂O valence electrons than do the ground state s electrons of the other configurations considered, i.e., the reaction barrier is smaller.⁴ This is also the basic reason why the s-p promotion energies have to be considered in the determination of the barriers.

In the above the Al, AlCl and BCl data all are from the AFOSR work, the Cu + N₂O result came from our NSF-supported studies, and the other data from the literature. Our further AFOSR work is in part aimed at establishing further correlations.

The significance of publication (in preparation) 9 is that these observations represent a new class of reactions, i.e., that between gaseous metal oxides and hydrocarbons. While the possibility for such reactions had been suggested, they had not yet been observed. Our equipment is uniquely suited for such observations. It would appear that many such reactions can occur. A further extension of this work is probably outside the scope of AFOSR's current interests, and our new AFOSR supported work, but its significance should be clearer when the results become generally known. For instance, reactions of this nature should lead to a better understanding of the mechanism of solid metal oxide catalyzed synthesis of higher hydrocarbons from methane.

III. PROFESSIONAL PERSONNEL

In addition to Professor A. Fontijn, the Principal Investigator, the following Ph.D. students have been involved with the work: A.G. Slavejkov, P.M. Futerko, and D.P. Belyung. In May 1990 Mr. Slavejkov successfully defended his Ph.D. thesis "Kinetic Studies of Reactions of BCl, AlCl and AlO with O₂, CO₂, Cl₂ and HCl over Wide Temperature Ranges". Mr. Futerko is currently preparing his Ph.D. thesis; the work is being continued by Mr. Belyung. In addition to these, Mr. W.F. Flaherty has rendered valuable assistance.

IV. 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, Boston College, Boston, MA (February 1989).
2. Department of Chemistry, Emory University, Atlanta, GA (February 1989).
3. Physical Chemistry Laboratory, Oxford University, Oxford, England (May 1989).
4. Department of Chemistry, The University of Southampton, Southampton, England (May 1989).
5. School of Chemistry and Department of Space Research, The University of Birmingham, Birmingham, England (May 1989).
6. Physical-Chemistry Institute, The University of Heidelberg, Heidelberg, W. Germany (June 1989).
7. Department of Chemistry, University of Reading, Reading, England (June 1989).
8. BP Research Centre, Sunbury-on-Thames, England (June 1989).
9. Shell Thornton Research Centre, Chester, England (June 1989).
10. Second International Conference on Chemical Kinetics, Gaithersburg, MD (July 1989).
11. Eastern Section, The Combustion Institute, Fall Technical Meeting, Albany, NY (October 1989).
12. National Research Council, Ottawa, Ontario, Canada (April 1990).
13. International Symposium on Combustion, Orleans, France (July 1990).
14. AFOSR/ONR Contractors Meeting on Propulsion, Atlanta, GA (June 1990) -- 2 presentations.
15. American Chemical Society, National Meeting, Washington, D.C. (August 1990).
16. NIEHS Conference on Health Effect of Combustion By-Products, Bethesda, MD (October 1990).
17. Department of Chemical Engineering and Materials Science, The University of Minnesota, Minneapolis, MN (October 1990).

18. Solid Waste Combustion Research Institute, Semi-Annual Meeting, Cornell University, Ithaca, NY (November 1990).
19. American Institute of Chemical Engineers, Chicago, IL (November 1990).
20. AFOSR Contractors Meeting in Propulsion, Boulder, CO (June 1991).
21. International Free Radicals Symposium, Williamstown, MA (August 1991).
22. American Chemical Society, National Meeting, New York, NY (August 1991).
23. American Institute of Chemical Engineers, Annual Meeting, Los Angeles, CA (November 1991).
24. Phillips Laboratory, Edwards AFB, CA (November 1991).

The last of these talks was held as part of discussions at the Phillips Laboratory about their work on HEDMs and other aspects of rocket propellant combustion and the utilization of our work therein. The principal hosts were Dr. S.L. Rodgers and D.P. Weaver. There have been frequent contacts with the latter throughout the three-year duration of this grant.

In addition to the many conversations with Air Force personnel at the Contractors Meetings, the following may be mentioned. A visit to our laboratory of Drs. M.A. Birkan and J.M. Tishkoff of AFOSR in October 1989 and my (A.F.) attendance that same month at the ONR workshop on "Energetic Solids Combustion Research", where I summarized the status of Al and B combustion kinetics in propellants.

Another significant series of interactions took place at the August 1991 American Chemical Society Meeting, for which I organized a four-day conference on "Gas-Phase Metal Reactions". This was apparently the first time that workers in various aspects of that field came together. The papers, revised after discussions at the meeting and subsequent refereeing, will appear in a volume by the same title published by Elsevier, with anticipated appearance in late summer or early fall of 1992. The insights obtained by juxtaposition of these various investigations have significantly advanced the understanding of the area and continues to stimulate research.

References

1. A. Fontijn and R. Zellner, "Influence of Temperature on Rate Coefficients of Bimolecular Reactions", Reactions of Small Transient Species, A. Fontijn and M.A.A. Clyne, Eds., (Academic Press, London, 1983), Chap. 1.
2. D.R. Yarkony, "On the Reaction $\text{Mg} + \text{N}_2\text{O} \rightarrow \text{MgO} + \text{N}_2$ ", *J. Chem. Phys.* **78**, 6763 (1983).
3. J.O. Hirschfelder, "Semi-Empirical Calculations of Activation Energies", *J. Chem. Phys.* **2**, 645 (1941).
4. P.M. Futerko and A. Fontijn, "Activation Barriers for Series of Exothermic Homologous Reactions. I. Metal Atom Reactions with N_2O ", *J. Chem. Phys.* **95**, 8065 (1991).