

REPORT DOCUMENTATION PAGE			Form Approved GMS No. 0704-0188
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 1998	3. REPORT TYPE AND DATES COVERED Final, March 1995-March 1998
4. TITLE AND SUBTITLE Wide Temperature Range Kinetics of Plume Reactions		5. FUNDING NUMBERS PE - 61102F PR - 2308 SA - AS G - F49620-95-1-0258	
6. AUTHOR(S) Arthur Fontijn		7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Rensselaer Polytechnic Institute High-Temperature Reaction Kinetics Laboratory The Isermann Department of Chemical Engineering Troy, NY 12180-3590	
9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NA 110 Duncan Avenue, Suite B115 Bolling AFB, DC 20332-0001		8. PERFORMING ORGANIZATION REPORT NUMBER	
11. SUPPLEMENTARY NOTES		10. SPONSORING MONITORING AGENCY REPORT NUMBER 19980618 045	
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The kinetics of reactions leading to the $\text{CO}(A^1\Pi-X^1\Sigma)$ Fourth Positive vacuum ultraviolet emission is studied for incorporation in plume radiation models. A fast-flow reactor and a high-temperature, pseudo-static, photochemistry reactor have been used. Experiments with the former on the $\text{O} + \text{C}_2\text{H}_2$ reaction have shown that the intensity of the $\text{CO}(d^3\Delta-a^3\Pi)$ Triplet bands decreases with increasing pressure. This is in accord with the proposed mechanism for $\text{CO}(A^1\Pi)$ formation, by collision-induced curve crossing from CO triplet states. Experiments in the pseudo-static reactor have confirmed the increase of the $\text{CO}(A^1\Pi-X^1\Sigma)$ chemiluminescence intensity with pressure, as indicated by this mechanism, but show a decrease in the intensity of the emission when the $\text{C}_2 + \text{O}_2$ reaction is investigated instead. This indicates a direct $\text{CO}(A^1\Pi)$ formation in the latter reaction, which leads to more intense vuv emission and may be a more important reaction for rocket exhausts. As the first step toward obtaining the absolute light intensities and chemiluminescence efficiencies for the $\text{C}_2 + \text{O}_2$ reaction, its vuv emission is used to obtain its overall rate coefficients, $k(300-976 \text{ K}) = 1.8 \times 10^{-11} \exp(-451 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These values are in excellent agreement with earlier experiments, where the C_2 consumption rate coefficients were measured instead.			
14. SUBJECT TERMS Rocket plumes, uv radiation, chemiluminescence, Reactions, C_2H_2 , O, C_2 , O_2		15. NUMBER OF PAGES 23	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		16. PRICE CODE	
18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
20. LIMITATION OF ABSTRACT UL			

TABLE OF CONTENTS

	<u>Page</u>
Research Objectives	1
Results and Publications	1
Presentations and Significant Interactions	2
Theses	3
Professional Personnel	3
References	3
Appendix A	ff 4
Arthur Fontijn, Mai Y. Randall, Abdellatif Goumri, and Paul E. Brock II, "Comparison of Mechanisms Leading to CO Fourth Positive System Vacuum Ultraviolet Chemiluminescence", AIAA Paper 98-3538.	
Appendix B	
A. Fontijn, "Wide-Temperature Range Observations on Reactions of Metal Atoms and Small Radicals", in High Temperature Materials Chemistry, K.E. Spear, Ed., The Electrochemical Society, Inc., Pennington, NJ, Proceedings Volume 97-39, 1997, pp. 617-628.	

RESEARCH OBJECTIVES

Optical detectors on satellites are used to observe missiles during their launch, ascent, and reentry phases. In principle, radiation from rocket plumes could be used to identify the type of fuel used on an incoming missile. However, insufficient information is available to allow developing models for quantitatively predicting uv plume signatures. Knowledge of rate coefficients and light yields of chemiluminescent reactions as functions of pressure and temperature is required. In the present work we have begun to provide these. In general, the target reactions are those of rocket exhaust species, such as CH, CH₂, C₂H₂, C₂, Al, and AlCl with atmospheric reactants, mainly O and O₂, as well as with H₂O. These are studied using our unique reactors of the HTFFR (high-temperature fast-flow reactor) and HTP (high-temperature photochemistry) types. In particular we have concentrated on the CO (A¹Π-X¹Σ) vacuum ultraviolet (vuv) emissions from the O + C₂H₂ and C₂ + O₂ reactions. Additionally, further work on metallic species reactions has been performed.

RESULTS AND PUBLICATIONS

The major experimental set-up, the experiments and the results from the C₂ and C₂H₂ chemiluminescence work have been described in detail in a recent publication: Arthur Fontijn, Mai Y. Randall, Abdellatif Goumri, and Paul E. Brock II, **"Comparison of Mechanisms Leading to CO Fourth Positive System Vacuum Ultraviolet Chemiluminescence"**, AIAA Paper 98-3538.

This paper is attached as **Appendix A**. A major conclusion from this work is that the C₂ + O₂ reaction, which had only been studied in passing by previous investigators, is a more likely major contributor to plume vuv emissions than the more widely studied O + C₂H₂ reaction. This conclusion corroborates one Dr. H.G. Wolfhard and I came to a few years ago in analyzing a series of plume¹ and other flame²⁻⁴ data, i.e. that the C₂ radical plays a major role in the production of many of the chemiluminescence emission features associated with the combustion of organic fuels. In current studies we are further investigating the C₂ + O₂ chemiluminescence.

Reactions of metallic species, particularly Al and its compounds, lead to plume

chemiluminescence⁵ and fluorescence⁶. Under a parallel AASERT grant⁷ we have studied reactions of such species. The detailed publications on that work will be discussed in the final report on that grant. An overview paper has also been prepared:

A. Fontijn, "Wide-Temperature Range Observations on Reactions of Metal Atoms and Small Radicals", in *High Temperature Materials Chemistry*, K.E. Spear, Ed., The Electrochemical Society, Inc., Pennington, NJ, Proceedings Volume 97-39, 1997, pp. 617-628.

This paper is attached as **Appendix B..** It will also appear in a collection of the invited papers of the Ninth International Conference on High Temperature Materials Chemistry, in *Pure and Applied Chemistry*.

PRESENTATIONS AND SIGNIFICANT INTERACTIONS

Presentations involving our AFOSR work have been given at:

- i) Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY (1995).
- ii) Army Research Laboratory, Aberdeen Proving Ground, MD (1995).
- iii) AFOSR Contractors Meeting, Regular Sessions, Chicago, IL (1995).
- iv) Same meeting, Workshop on Aerothermochemistry of High Altitude Plumes" (1995).
- v) CNRS Laboratory for Photophysics and Molecular Photochemistry, Bordeaux, France (1995).
- vi) Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada (1996).
- vii) AFOSR Contractors Meeting, Hampton University, Hampton, VA (1996).
- viii) Department of Chemical Engineering, The University of Connecticut, Storrs, CT (1996).
- ix) Department of Mechanical Engineering, The Ohio State University, Columbus, OH (1996).
- x) Air Force Phillips Laboratory, Hanscom AFB, MA (1997).
- xi) Ninth International Conference on High-Temperature Materials Chemistry, Pennsylvania State University, State College, PA (1997).

- xii) AFOSR Contractors Meeting, San Diego, CA (1997).
- xiii) Fourth International Conference on Chemical Kinetics, NIST, Gaithersburg, MD (1997).

In the course of this work we have had extensive discussions on plume radiation problems and research with:

Drs. H.G. Wolfhard, and D.A. Levin, IDA, Alexandria, VA.

Dr. D.P. Weaver, Air Force Research Laboratories, Propulsion Directorate

Drs. L.S. Bernstein and W.L. Dimpfl, Spectral Sciences, Inc.

Drs. J.W. Rich and V.V. Subramaniam, Mechanical Engineering, Ohio State University

Dr. E. Murad, Air Force Research Laboratory, Geophysics Directorate.

In addition, we advised Dr. A.A. Viggiano and his group at the Geophysics Directorate on the design of a high temperature reactor for study of ionospheric effects.

THESES

The following theses have resulted in part from support under the present grant:

D.P. Belyung, "Kinetics of Metal Combustion Reactions", Ph.D., Rensselaer Polytechnic Institute, May 1997.

G.T. Dalakos, "BO Reactions Over a Wide Temperature Range", Rensselaer Polytechnic Institute, May 1996.

PROFESSIONAL PERSONNEL

In addition to Dr. Belyung and Mr. Dalakos, Dr. A. Goumri, a postdoctoral fellow, A. Fernandez, a Ph.D. student, M.Y. Randall, an MS student, P.E. Brock, an undergraduate research assistant, and W.F. Flaherty, our group technician, have contributed to the work.

REFERENCES

1. H.G. Wolfhard, in *Handbook on Ballistic Missile Plume Signatures* (U), Vol. 3, Ultraviolet and Visible Emission of Plumes (U).
2. A.G. Gaydon and H.G. Wolfhard, *Flames. Their Structure, Radiation and Temperature*. 4th ed., Chapman and Hall, London, 1979.
3. A.G. Gaydon, *The Spectroscopy of Flames*, 2nd ed., Chapman and Hall, London,

1974.

4. A. Fontijn, Ed. *Gas-Phase Chemiluminescence and Chemi-Ionization*, North Holland, Amsterdam, 1985.
5. D.J. Knecht, C.P. Pike, E. Murad, and D.L. A. Rall, "Interaction of Solid-Rocket Exhaust with the Atmosphere", *J. Spacecraft and Rockets* 33, 677 (1996).
6. L.S. Bernstein, "Analysis of UV-Visible Boostphase Plume Observations from the MSX MDT11 Mission" (U), JANNAF Exhaust Plume Technology Meeting, April 1997.
7. A. Fontijn, "Student Research in Rocket and Plume Reaction Kinetics", AFOSR Grant F49620-95-1-0473, 1 August 1995-31 July 1998.

APPENDIX A



AIAA98-3538
Comparison of Mechanisms
Leading to CO Fourth Positive
System Vacuum Ultraviolet
Chemiluminescence

Arthur Fontijn, Mai Y. Randall, Abdellatif Goumri, and
Paul E. Brock II
Rensselaer Polytechnic Institute
Troy, NY 12180-3590

34th AIAA/ASME/SAE/ASEE
Joint Propulsion Conference & Exhibit
July 13-15, 1998 / Cleveland, OH

COMPARISON OF MECHANISMS LEADING TO CO FOURTH POSITIVE
SYSTEM VACUUM ULTRAVIOLET CHEMILUMINESCENCE

Arthur Fontijn*, Mai Y. Randall,† Abdellatif Goumri,§ and Paul E. Brock ¶
Rensselaer Polytechnic Institute, Troy, NY 12180-3590.

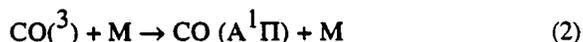
ABSTRACT

The kinetics of reactions leading to the $\text{CO}(A^1\Pi-X^1\Sigma)$ Fourth Positive vacuum ultraviolet emission is studied for incorporation in plume radiation models. A fast-flow reactor and a high-temperature, pseudo-static, photochemistry reactor have been used. Experiments with the former on the $\text{O} + \text{C}_2\text{H}_2$ reaction have shown that the intensity of the $\text{CO}(d^3\Delta-a^3\Pi)$ Triplet bands decreases with increasing pressure. This is in accord with the proposed mechanism for $\text{CO}(A^1\Pi)$ formation, by collision-induced curve crossing from CO triplet states. Experiments in the pseudo-static reactor have confirmed the increase of the $\text{CO}(A^1\Pi-X^1\Sigma)$ chemiluminescence intensity with pressure, as indicated by this mechanism, but show a decrease in the intensity of the emission when the $\text{C}_2 + \text{O}_2$ reaction is investigated instead. This indicates a direct $\text{CO}(A^1\Pi)$ formation in the latter reaction, which leads to more intense vuv emission and may be a more important reaction for rocket exhausts. As the first step toward obtaining the absolute light intensities and chemiluminescence efficiencies for the $\text{C}_2 + \text{O}_2$ reaction, its vuv emission is used to obtain its overall rate coefficients, $k(300-976 \text{ K}) = 1.8 \times 10^{-11} \exp(-451 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These values are in excellent agreement with earlier experiments, where the C_2 consumption rate coefficients were measured instead.

INTRODUCTION

Optical detectors on satellites are used to observe missiles during their launch, ascent, and reentry phases. In principle, radiation from rocket plumes could be used to identify the type of fuel used on an incoming missile. However, insufficient information is available to quantitatively predict uv plume signatures. Knowledge of rate coefficients and light yields from potentially competing mechanisms is required. We report here on the status of a program to provide the missing reaction kinetic information over wide temperature and pressure ranges. Particularly, the $\text{CO}(A^1\Pi-X^1\Sigma)$ Fourth Positive (4+) emission from the $\text{O} + \text{C}_2\text{H}_2$ and $\text{C}_2 + \text{O}_2$ reactions are discussed and compared.

The $\text{O} + \text{C}_2\text{H}_2$ reaction is a rich source of chemiluminescent emissions and involves two species present in high-altitude plumes from, respectively, the atmosphere and the fuel. The spectral distribution of the main mechanism leading to the CO 4+ emission has been identified in a number of studies.¹⁻⁴ The $\text{O} + \text{C}_2\text{H}_2$ reaction leads to formation of C_2O followed by:



Here $\text{CO}({}^3)$ represents triplet states of CO , emissions from which are also observed from these reactions.²⁻⁵ Pressure-dependence¹ and time-resolved³ data have shown the necessity of including step (2). As a corollary, inclusion of this step indicates that the triplet bands should have the opposite pressure dependence from the 4+ bands. This needs to be verified. A schematic presentation of the CO potential curves and transitions is given in Figure 1. A more detailed CO diagram showing vibrational levels may be found in Ref. 6.

One problem with the above scheme is that the maximum energy available from the $\text{O} + \text{C}_2\text{H}_2$ reaction is only 9.8 eV, which is 0.3 eV less than needed for population of the highest observed vibrational levels. This has been explained by energy transfer processes, or collisions at the

Copyright © 1998 by Arthur Fontijn, Published by the American Institute of Aeronautics and Astronautics, Inc. with permission.

*Professor and Chairman, The Isermann Department of Chemical Engineering, not an AIAA Member.

†Graduate student, The Isermann Department of Chemical Engineering, not an AIAA Member

§Postdoctoral Fellow, current address, Department of Chemistry, The University of North Texas, Denton, TX, not an AIAA Member

¶Undergraduate Research Assistant, The Isermann Department of Chemical Engineering, not an AIAA Member

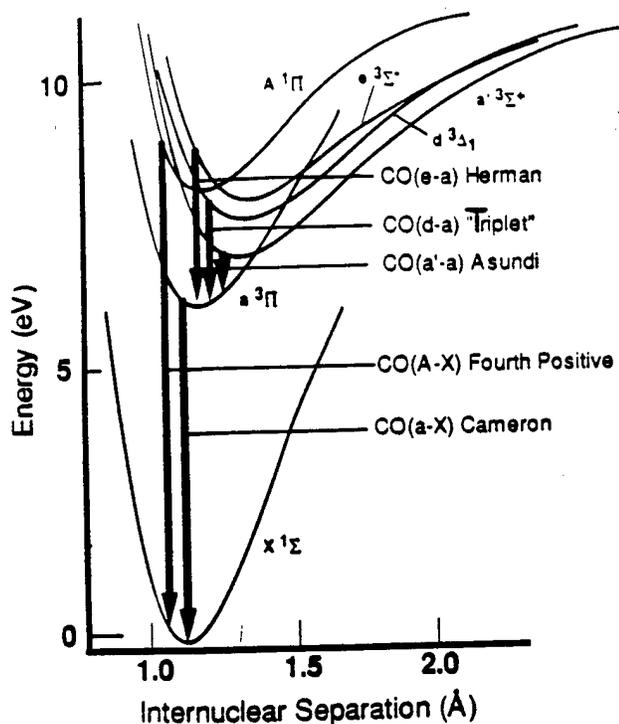


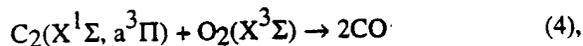
Fig. 1 CO potential curves and transitions. Generated by W.L. Dimpfl, Spectral Sciences, Inc., from scaled traces of Fig. 3 of Tilford and Simmons⁶.

tail end of the Boltzmann distribution. However, it is unlikely that the 9.8 eV reaction energy remains available through the series of steps leading to $A^1\Pi$ formation. Additional mechanisms need to be considered.

The reaction



could supply 11.1 eV, more than is required for the observed $CO(A^1\Pi)$ excitation. However, it has been shown that this reaction can not be important in flames^{1,2} and a three-body reaction could also not be significant at high altitudes. It has been established that^{7,8,9}



which is 10.84 and 10.92 eV exothermic, for $C_2(X^1\Sigma)$ and $C_2(a^3\Pi)$, respectively, leads to both $CO(^3)$ and vuv, i.e. $A^1\Pi$, emissions. These two states of C_2 are close together, separated by 0.08 eV, and rapidly equilibrate in the presence of $O_2(X^3\Sigma)$.¹⁰ To form $CO(A^1\Pi)$ the energetics require that the second CO is in the $X^1\Sigma$ state. Thus, spin conservation demands that only $C_2(a^3\Pi)$ is directly

involved in the 4+ emission, whereas both C_2 states could form the triplet states. The exothermicity of this reaction is such that no further assumptions are necessary to explain the 4+ emissions. This mechanism appears less complex than that involving reactions (1) and (2), and no third body is involved. In addition to contributing to the 4+ emission from reactions (1) and (2) over the whole wavelength range, reaction (4) could be exclusively responsible for the formation of the highest vibrational levels of $CO(A^1\Pi)$. In rocket plumes, C_2 could be present from the rich combustion in the chamber. Prior to the present work little was known of the CO 4+ emission from reaction (4). Assignment of the vuv emission to the 4+ system is likely, but unconfirmed. There are no reported absolute light intensity measurements and there was no information on the influence of pressure and temperature on the emissions. In the present work we have begun to provide such information.

Here we report on the influence of pressure on the 4+ and Triplet emissions from $O + C_2H_2$. The influence of pressure on the wavelength integrated vuv emissions from reaction (4) is compared to that of the $O + C_2H_2$ reaction and the temperature dependent overall rate coefficients of reaction (4) are measured. Work on the comparison of the spectral distributions of the respective vuv emissions is in progress.

CO CHEMILUMINESCENCE FROM THE $O + C_2H_2$ REACTION

Our earlier experiments have shown that the CO 4+ bands intensity increases with increasing pressure from about 1 to 10 mbar. This is explained by adding reaction (2) to the mechanism, i.e. by involving a collision-induced crossing from triplet potential curves.¹ The resulting depletion of molecules in triplet states should lead to a decrease in the intensity of triplet states emission. We have now performed experiments to check this. The $O + C_2H_2$ spectrum is very rich in the region of the triplet state emissions, where intense $CH(A^2\Delta-X^2\Pi)$ 430 nm system and $C_2(A^3\Pi-X^3\Pi)$ Swan system emissions are present. We have chosen to perform these experiments on the $(d^3\Delta-a^3\Pi)$ "Triplet" system, which can best be distinguished from these emissions.

The experiments were performed at room temperature in a Pyrex fast-flow reactor, Figure 2, of very similar design and operation to that of Ref. 1. Oxygen atoms were produced by passing 5.00% O_2 (Scott Analyzed) in Ar through a microwave discharge. Downstream, C_2H_2 (99.6%, Liquid Carbonic) was introduced through a moveable inlet. Spectral measurements were obtained using a Minuteman 305-M monochromator equipped with a Centronic 4283 TIR photomultiplier tube (PMT).

Measurements have been made on the $CO(d-a)$ (8,0), (7,0), (6,0), (5,0), and (3,0) bands. Figure 3 shows the spectrum of the former band. Intensity data were obtained

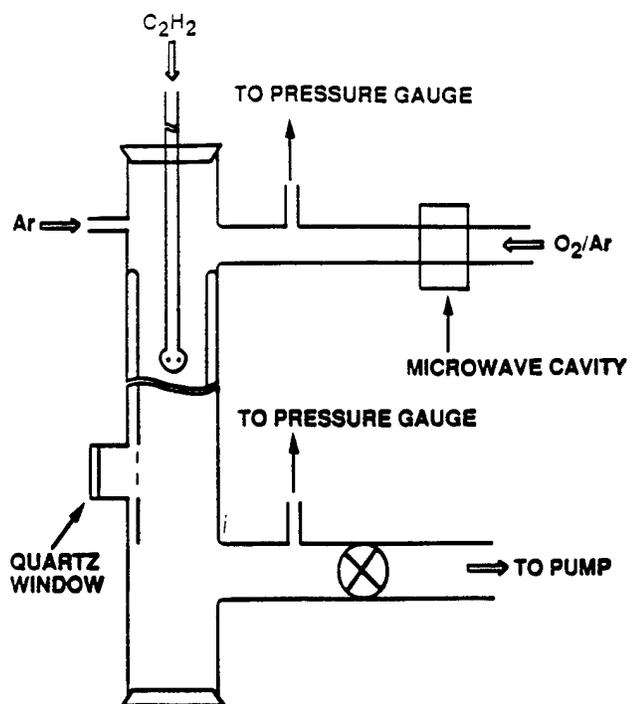


Fig. 2: The Pyrex fast-flow reactor.

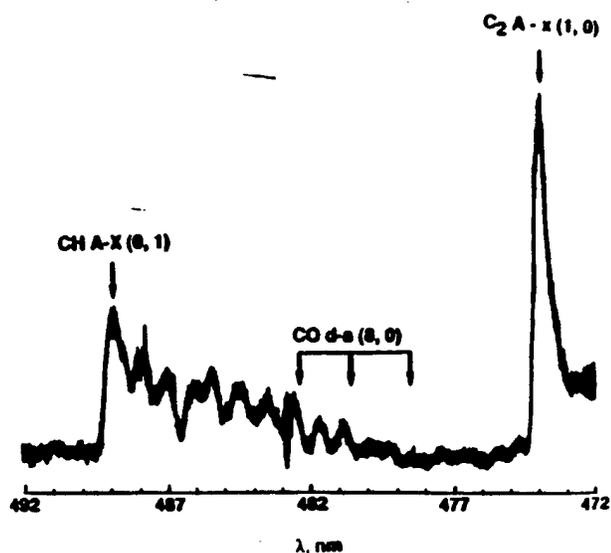


Fig. 3: Spectral distribution of the $O + C_2H_2$ chemiluminescence from 492 to 472 nm. $P = 2.0$ mbar, $[O] = 2.7 \times 10^{14}$ atoms cm^{-3} , $[C_2H_2] = 9.2 \times 10^{14}$ molecules cm^{-3} , $\bar{v} = 6$ m s^{-1} .

in two different ways, (i) by subtracting the detector background, here the intensity of the 492-490 nm range, and (ii) by subtracting the contours of the underlying CH or C_2 bands. The resulting intensities were plotted against reaction time at a number of pressures, as shown in Figure 4 for the (8,0) band at 480.7 nm. In these experiments the pump was throttled, thus decreasing the average gas

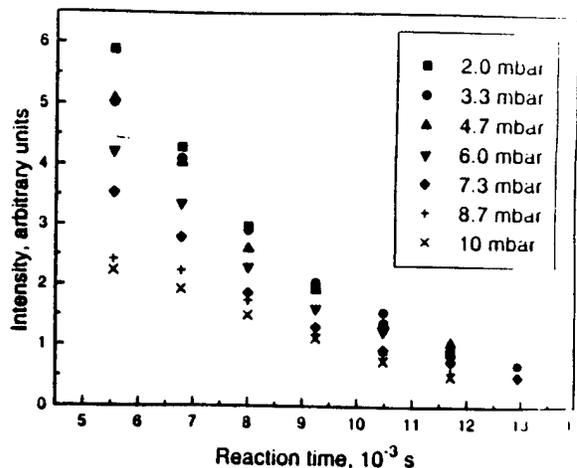


Fig. 4: Fast-flow reactor measurements of the intensity of the $CO(d-a, 8-0)$ emission vs. reaction time, as a function of pressure. Reactant concentrations as in Fig. 3.

velocity \bar{v} , but the reactant concentrations were kept constant. The $[O]$ was kept constant by shutting the C_2H_2 flow off, adding a known $[NO]$ and adjusting the microwave discharge power so that the light intensity of the $O+NO \rightarrow NO_2 + hv$ reaction was the same at all pressures.¹¹ The absolute $[O]$ of Figures 3 and 4 was obtained by using the $N + NO \rightarrow N_2 + O$ titration reaction.¹²

The areas under the plots of Figure 4 represent the time-integrated intensities. A graph of these areas versus pressure is given in Figure 5. The slope of this plot, dI/dP is $(-8.1 \pm 0.4) \times 10^{-2}$ mbar $^{-1}$. In Table I this is compared to the slopes from the other bands measured, obtained in the same fashion. It may be seen that all decrease similarly with pressure and the results are essentially independent of the intensity subtraction method used. As a further check on the reliability of the intensity measurement methods used, the pressure dependence of the underlying CH and C_2 bands was measured. They were found to be independent of pressure.

The results are in accord with the reactions (1) and (2) scheme. Other triplet states could also be involved in the $A^1\Pi$ population. The $CO(d)$ vibrational levels studied all represent adequate energies to transfer to the $A^1\Pi$ state. The $d, v < 3$ levels have insufficient energy to cross over to the $A^1\Pi$ potential curve, though they could energy-pool with some third bodies. It would be interesting to investigate similarly the dI/dP for these lower levels.

The opposite pressure dependence of the Triplet and 4+ bands also indicates that in this reaction system the $d^3\Delta$ and $A^1\Pi$ levels are not formed by collision-induced transitions from a common precursor, such as $CO(X^1\Sigma, v=high)$.

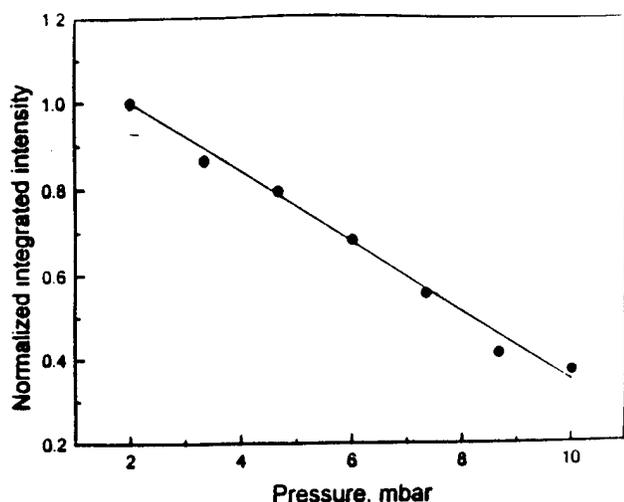


Fig. 5: Time-integrated intensities of the measurements of Fig. 4 versus pressure.

Table I. Influence of pressure on CO (d-a) Triplet emissions

Wavelength, nm	$\frac{dI}{dP}$, $10^{-2} \text{ mbar}^{-1}$
480.7 (8,0)	-8.1 ± 0.4^a
	-8.1 ± 0.4^b
505.3 (7,0)	-7.6 ± 0.9^a
	-7.6 ± 0.9^b
533.0 (6,0)	-6.8 ± 0.6^a
	-6.8 ± 0.6^b
567.0 (5,0)	-5.9 ± 0.8^a
	-6.3 ± 0.8^b
640.1 (3,0)	-7.5 ± 0.3^a
	-7.5 ± 0.3^b

a) From baseline subtraction

b) From CH(A-X) and C₂(A-X) contours subtraction

COMPARISON OF THE CHEMILUMINESCENCE INTENSITIES FROM O + C₂H₂ AND C₂ + O₂

To study reaction (4), the transient species C₂ needs to be produced. A number of experimental approaches have been explored. In one of our high-temperature photochemistry (HTP) reactors, Figure 6, C₂ was produced using 193 nm multiphoton excimer laser photolysis of

C₂Cl₄ or C₂H₂.¹³ (In preliminary experiments C₂H₄ was similarly used). HTP reactors operate in a pseudo-static pulsed mode. The slow flow used is fast enough to provide each photolysis pulse with a fresh reactant mixture and the residence times are long compared to the reaction times. The observations are made from the center of the reaction zone and are not influenced by wall interference. The bath gas temperature determines that of the reaction and the reactants are introduced through a cooled inlet as shown. At the temperatures used here, this inlet is not an essential feature.

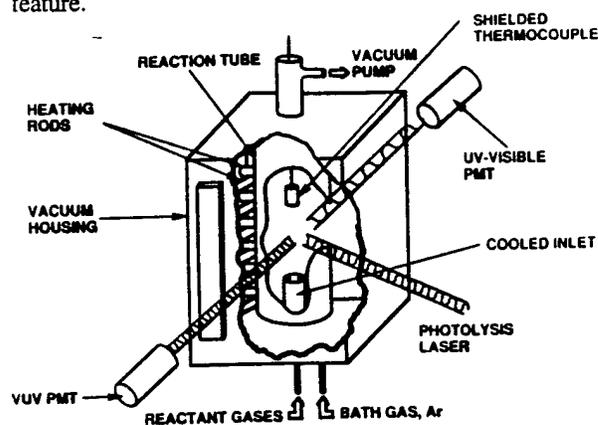


Fig. 6 The HTP reactor as used for comparison of the C₂ + O₂ to O + C₂H₂ wavelength-integrated vuv intensities, and the O + NO pressure-dependence calibrations.

The other reactor to be employed, to produce C₂, is a high-temperature fast-flow reactor (HTFFR), which allows for steady state observations similar to the work of Section 2. Here C₂Cl₄ is passed over heated potassium, which results in C₂Cl₄ + 4K → C₂ + 4KCl.¹⁴ This method is shown in Figure 7. To test this method, the reactor of Figure 2 was used. Both the HTP and HTFFR reactor types and their operation have been described previously.¹⁵ In both, the pseudo-static and fast-flow reactors, addition of O₂ led to the vuv emission.

For spectral distribution measurements in either reactor, the monochromator PMT combination of Section 2 is not suitable, as (i) the HTP chemiluminescence is pulsed and (ii) the fast-flow reactor signal decreases with time and could be maintained only for about 20 minutes, due to depletion of the potassium. For spectral observation under these conditions, a CCD detector (Princeton Instruments, TE/CCD-1024 EVUV) has been acquired and is currently being calibrated. With this detector, intensities over wide spectral ranges, e.g. 40 nm, can be obtained in either reactor and the monochromator does not need to be scanned, contrary to operation with PMTs. Measurements with the CCD camera will be forthcoming shortly. Here we report on the pressure dependence of the 110 to 200 nm spectrally-integrated emission intensities, obtained with a solar blind vuv PMT (Thorn EMI G26E314LF), connected to the HTP reactor through a MgF₂ window.

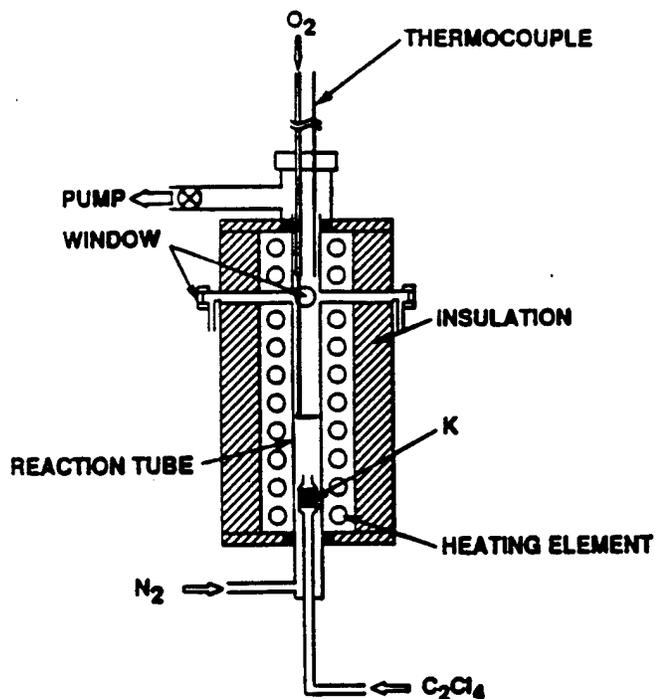


Fig. 7: The HTFFR, as configured for C_2 experiments.

HTP reactors have been used for rate coefficient measurements. Reactors of this type have not previously been used for light intensity comparisons. To verify that measurements of the pressure dependence of emissions can be made in such reactors, the pressure dependence of the 4+ emission from the $O + C_2H_2$ reaction was first measured and compared to that obtained previously in a fast-flow reactor.¹ The O atoms were produced from 193 nm single-photon photolysis of SO_2 . The observation zone is geometrically restricted and an increase in pressure will cause an increased amount of the reaction events to be observed, which would falsify pressure-dependence observations. To eliminate this problem, the vuv emission from $O + C_2H_2$ and the uv visible emission from the pressure-independent¹¹ reaction $O + NO \rightarrow NO_2 + hv$ were measured alternately. As shown in Figure 6, the latter was measured with a uv-visible PMT (Thorn EMI 9813QB). The intensity ratio $I(CO\ 4+)/I(NO_2)$ then approximates the true pressure-dependence. Figure 8 shows the result, which is very similar to that of the earlier flow tube study, i.e. a rise in intensity with pressure and a leveling out above about 10 mbar.

A $C_2 + O_2$ result in the same pressure domain is given in Figure 9. For this figure C_2H_2 was used as the photolyte; similar results were obtained when C_2Cl_4 was used. No intensity increase with increasing pressure is seen in these experiments, which suggests that here $CO(A^1\Pi)$ is formed directly, not via an intersystem crossing from triplet

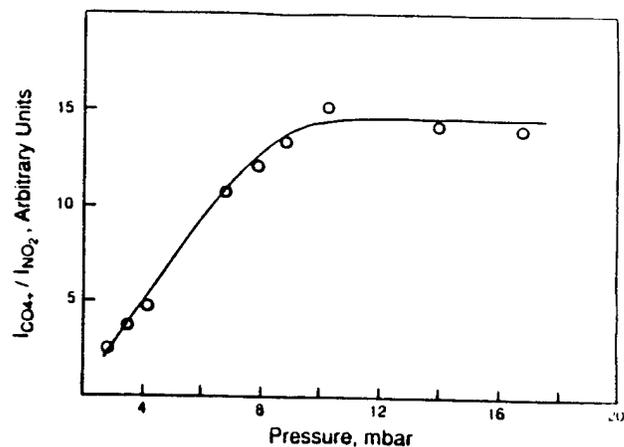


Fig. 8: HTP measurements of the wavelength-integrated CO 4+ intensity versus pressure for the $O + C_2H_2$ reaction. $T = 300\text{ K}$, $[SO_2] = 9.9 \times 10^{12}$ molecules cm^{-3} , $[C_2H_2] = 3.2 \times 10^{14}$ molecules cm^{-3} .

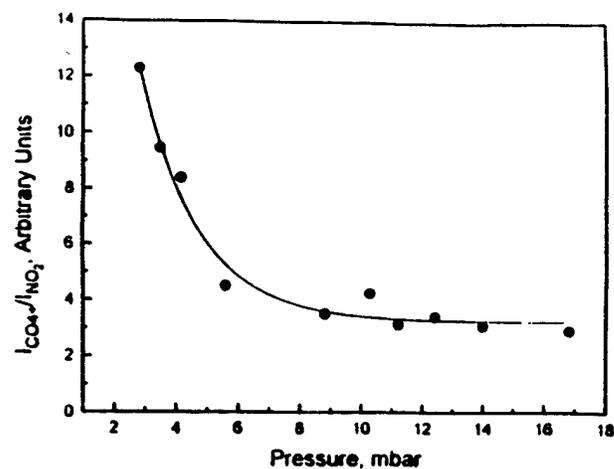


Fig. 9: HTP measurements of the wavelength-integrated CO 4+ intensity versus pressure for the $C_2 + O_2$ reaction. $T = 300\text{ K}$. $[C_2H_2] = 3.5 \times 10^{13}$ molecules cm^{-3} , $[O_2] = 5.3 \times 10^{14}$ molecules cm^{-3} .

states, which makes it all the more a likely important mechanism for plume radiation. Figure 9 actually shows an initial decrease in the CO 4+ intensity. This was first thought to be due to vibrational relaxation of $C_2(a^3\Pi)$. It is known that the overall (all product states) reaction (3) proceeds at room temperature about twice as fast for C_2 in the $v=1$ and 2 states, than for $v=0$, but that this difference disappears with increasing temperature.¹⁶ Measurements were therefore made at 740 K, about the highest temperature where the $O + NO$ emission was not significantly interfered with by wall radiation. The decrease

was still present and even more pronounced, Figure 10. Further experiments, including the detailed spectral distribution, would be required to explain this negative pressure dependence. The gases used in these experiments were Ar bath gas (Liquefied Ar of 99.998% purity, Matheson), 5.00% O₂ (Scott Analyzed), C₂H₂ (99.6% purity, Matheson), NO (99% purity, Matheson), and SO₂ (99.98% purity, Matheson). Mixtures of C₂Cl₄ (99.9+% HPLC grade, Sigma-Aldrich) in Ar were made in the laboratory.

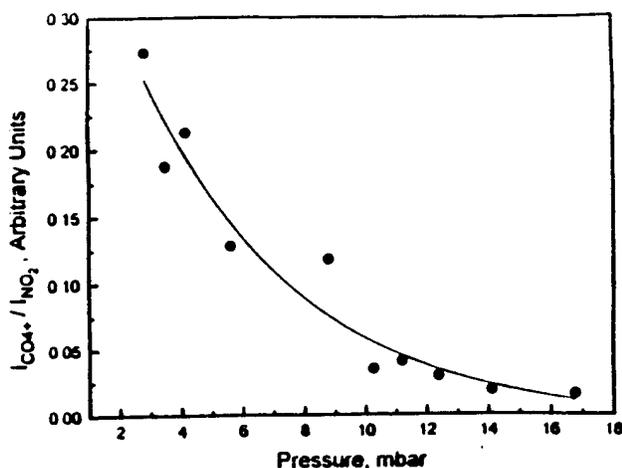


Fig. 10: HTP measurements of the wavelength-integrated CO 4+ intensity versus pressure for the C₂ + O₂ reaction. T = 740 K. [C₂Cl₄] = 5.9 × 10¹² molecules cm⁻³; [O₂] = 1.2 × 10¹⁴ molecules cm⁻³.

When C₂H₂ is used as the C₂ precursor, C₂H will also be formed, as it is known to be produced by single-photon photolysis.^{17,18} A few single-photon 193 nm experiments were therefore performed on C₂H₂/O₂/Ar mixtures, similar to those used in the above experiments. No vuv emission was observed. Thus the observed vuv emissions can be attributed to the C₂ reaction. Of course, C₂H could not have been present in the C₂Cl₄ photolysis or HTFFR experiments.

The intensities obtained from the C₂ + O₂ reaction were about an order of magnitude higher than those from the O + C₂H₂ reaction. This suggests the former to be an efficient process. The rate coefficient for light emission for the latter has been determined at room temperature.¹⁹

LIGHT EMISSION EFFICIENCY OF THE C₂ + O₂ REACTION

To determine the efficiency of reaction (4) as a light emitting process, a number of measurements are needed and some definitions are required. Absolute intensity is given by

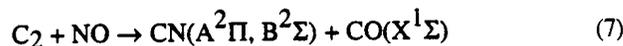
$$I = d[h\nu]/dt = k_{hv}[C_2][O_2] \quad (5)$$

where $h\nu$ represents a light quantum. The rate coefficients for light emission are related to the overall reaction rate coefficients $k(T)$ by the relation

$$k_{hv}(T) = \Phi(T)k(T) \quad (6)$$

where $\Phi(T)$ is the efficiency factor for light emission.

Determinations of absolute quantum yields from first principles are very time consuming. However, since those for the O + C₂H₂ reaction have been measured,¹⁹ those for C₂ + O₂ can be obtained by comparison.¹¹ In contrast to $k(T)$ measurements, which require absolute concentrations only of the reactant in excess, Equation (5) requires the absolute concentration of the limiting reactant, C₂, to be known as well. The absolute O₂ concentrations are obtained directly from flow rate and pressure measurements. Using fast-flow reactors, the absolute concentrations of transient species can be obtained by gas-phase titrations, which require a fast reaction and an indicator.¹² While developed for room temperature, this technique can be used equally well at high temperatures in HTFFRs.²⁰ For the determination of [C₂], the fast reaction²¹



would be used with the CN(B-X) and (A-X) emissions as indicators.

As the first step toward obtaining $\Phi(T)$, we are measuring $k(T)$ of the C₂ + O₂ reaction. The HTP reactor of Figure 6 is used for this work. C₂Cl₄ was used for the C₂ generation and 5.00% O₂ (Scott Analyzed), 0.50% O₂ (Matheson Analyzed), and O₂ (99.98% UHP, Matheson) mixtures with He (99.999% UHP, Matheson) made in the laboratory were used as sources of O₂. The procedures for obtaining rate coefficients have been described.¹⁵ The measurements have thus far spanned the 300-976 K range. The results are given in Table II. They may be seen to be independent of pressure, P, the corresponding total gas concentration (essentially Ar), [M], the average gas velocity

\bar{v} between the cooled inlet and the observed reaction zone (distance z), and the source of the O₂ used. The resulting rate coefficients are plotted in Figure 11. Over this temperature range they are well-fitted by the expression $k(T) = 1.8 \times 10^{-11} \exp(-451 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

In Figure 12 the present $k(T)$ results are compared to earlier measurement obtained under different conditions. The most extensive of these are those of Baughcum and Oldenberg.¹⁶ These are based on laser-induced fluorescence (LIF) measurements of the C₂(a³Π) consumption rates, which they found to be approximately equal to the C₂(X¹Σ) consumption rates, also measured by LIF. In that

Table 2: Summary of Rate Coefficient Measurements on the $C_2 + O_2$ Reaction

T, K	P, mbar	[M], 10^{18} cm^{-3}	$[C_2Cl_4]$, 10^{13} cm^{-3}	$[O_2]$ range, 10^{14} cm^{-3}	k , $\text{cm}^3 \text{ s}^{-1}$	z, cm	$k \pm \sigma_k$, $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
300	339	8.17	2.13	9.27 - 67.4 ^a	1.6	18	3.73 ± 0.54
310	112	2.61	1.25	2.04 - 7.78 ^b	7.0	23	4.86 ± 0.61
348	204	4.24	2.13	2.98 - 10.0 ^b	4.8	23	5.56 ± 0.38
386	139	2.60	2.40	4.08 - 15.6 ^c	4.4	23	6.17 ± 0.37
401	279	5.03	1.87	4.58 - 17.3 ^b	3.2	23	5.18 ± 0.50
426	141	2.40	0.35	1.82 - 13.3 ^a	8.2	19	6.30 ± 0.66
497	276	4.02	1.92	3.33 - 12.9 ^c	4.4	23	6.75 ± 0.34
584	256	3.17	1.77	2.03 - 7.79 ^b	7.0	23	8.23 ± 0.17
836	143	1.24	0.50	1.12 - 4.25 ^b	12.8	23	11.31 ± 0.88
976	109	0.81	0.57	0.57 - 2.18 ^b	25.2	23	12.23 ± 0.26

^a An analyzed 5.00% O_2 in Ar cylinder was used.

^b An analyzed 0.50% O_2 in Ar cylinder was used.

^c O_2/He mixtures (about 1% O_2) made in the laboratory for each experiment separately.

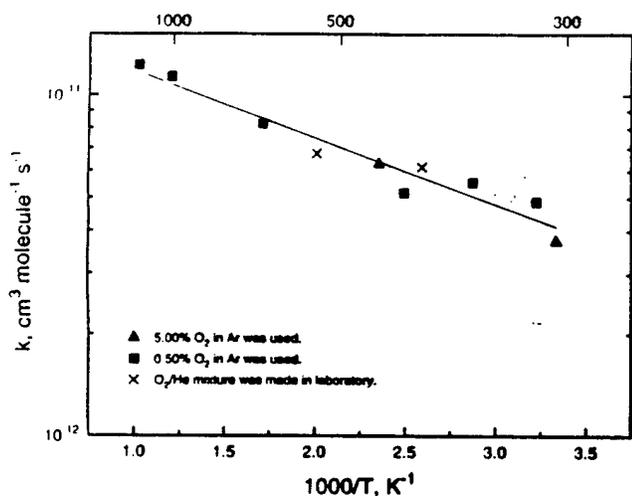


Fig. 11 Arrhenius plot of the present $C_2 + O_2$ rate coefficient measurements.

work CF_3CCCF_3 was used as the photolytic precursor of C_2 . Only one pressure, 20 mbar, considerably lower than that of the present work, was used. The results are in very good agreement with that of the current measurements, which are based on the vuv light emission production. Their $k(T)$ expression $1.5 \times 10^{-11} \exp(-493K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ agrees to within 30% with the present results, typical for the accuracy limits in such $k(T)$ determinations. Also shown in Figure 12 are the 300-600 K measurements by Pitts et al.,²² based on LIF observation of $C_2(X^1\Sigma)$ disappearance, and the room temperature measurements of Reisler et al.⁸ where CO triplet chemiluminescence was used as the diagnostic tool, and those of Filseth et al.⁹ who also used LIF on $C_2(a^3\Pi)$. All agree very well.

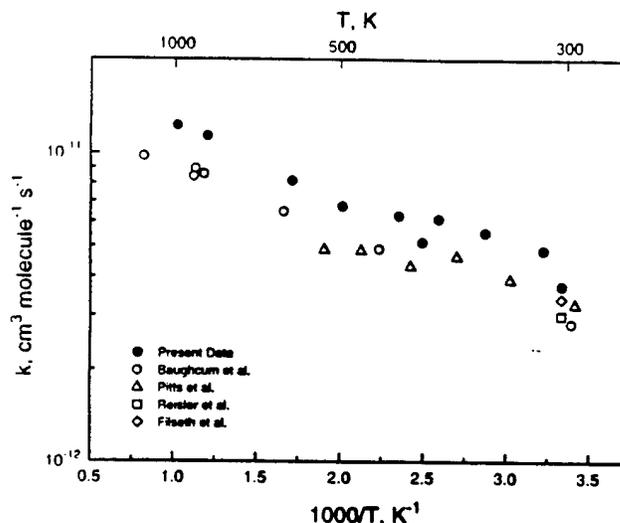


Fig. 12 Comparison of the present $C_2 + O_2$ measurements to those of earlier works. Data from Baughcum, et al.¹⁶, Pitts, et al.²², Reisler, et al.⁸, and Filseth, et al.⁹

The present rate coefficient measurements will be extended to higher temperatures (probably to about 1500 K) and will be combined with measurements of the absolute intensities and with C_2 titration values to obtain $\Phi(T)$. While the HTP reactor is the most suitable for rate coefficient measurements of C_2 reactions, these further measurements will require the use of the HTFFR.

CONCLUSIONS

Experiments on the $O + C_2H_2$ and $C_2 + O_2$ chemiluminescent reactions have been performed. Observations on the triplet emissions from the former have confirmed our previously proposed mechanism¹ for the formation of CO molecules in the $A^1\Pi$ state, which is

responsible for the vacuum ultraviolet emission from this reaction. The results obtained on the second reaction, for which less kinetic and no vuv spectroscopic information is available in the literature, suggest it is a less complex, attractive alternative mechanism for rocket exhaust vuv emissions.

ACKNOWLEDGEMENTS

This work is supported by AFOSR under grants F 49620-95-1-0258, F 49620-98-1-0047, and F 49620-95-1-0473. We thank Drs. D.P. Weaver and I.J. Wysong (Air Force Research Laboratories, Propulsion Directorate) for helpful comments in the course of this work, A. Fernandez for critically reading this manuscript, and W.F. Flaherty for assistance with some of the measurements.

REFERENCES

- 1 A. Fontijn and S.E. Johnson, "Mechanism of CO Fourth Positive VUV Chemiluminescence in the Atomic Oxygen Reaction with Acetylene. Production of $C(^3P, ^1D)$ ", *J. Chem. Phys.* **59**, 6193 (1973).
- 2 K.H. Becker and K.D. Bayes, "CO Chemiluminescence from Flames", *J. Chem. Phys.* **48**, 653 (1968).
- 3 W. Bauer, K.H. Becker, and R. Meuser, "Laser-Induced Fluorescence Studies on C_2O and CH Radicals", *Ber. Bunsenges, Phys. Chem.* **89**, 340 (1985).
- 4 K.D. Bayes, "Spectroscopic Study of the Chemiluminescent Reaction $O + CCO$ ", *J. Chem. Phys.* **52**, 1093 (1970).
- 5 M.L. Burke, W.L. Dimpfl, P.M. Sheaffer, P.F. Zittel, and L.S. Bernstein, "Formation of Triplet CO in Atomic Oxygen Flames of Acetylene and Carbon Suboxide", *J. Phys. Chem.* **100**, 138 (1996).
- 6 S.G. Tilford and J.D. Simmons, "Atlas of the Observed Absorption Spectrum of Carbon Monoxide Between 1060 and 1900Å", *J. Phys. Chem. Ref. Data* **1**, 147 (1972).
- 7 H. Reisler and C. Wittig, "Electronic Luminescence Resulting From Infrared Multiphoton Excitation", *Photoselective Chemistry*, Part I, J. Jortner, R.D. Levine, and S.A. Rice, Eds. (Wiley, New York, 1981), p. 679.
- 8 H. Reisler, M.S. Mangir, and C. Wittig, "The Kinetics of Free Radicals Generated by IR Laser Photolysis. II. Reactions of $C_2(X^1\Sigma)$, $C_2(a^3\Pi)$, $C_3(X^1\Sigma)$ and $CN(X^2\Sigma)$ with O_2 ", *Chem. Phys.* **47**, 49 (1980).
- 9 S.V. Filseth, G. Hancock, J. Fournier, and K. Meter, "Quenching of $C_2(a^3\Pi_u)$ Produced in an Intense Infrared Laser Field", *Chem. Phys. Lett.* **61**, 288 (1979).
- 10 M.S. Mangir, H. Reisler, and C. Wittig, "The Kinetics of Free Radicals Generated by IR Laser Photolysis. III. Intersystem Crossing between $C_2(X^1\Sigma)$ and $C_2(a^3\Pi)$ by Collision with Oxygen", *J. Chem. Phys.* **73**, 829 (1980).
- 11 A. Fontijn, C.B. Meyer and H.I. Schiff, "Absolute Quantum Yield Measurements of the NO-O Reaction and Its Use as a Standard for Chemiluminescent Reactions", *J. Chem. Phys.* **40**, 64 (1964).
- 12 A. Fontijn, D. Golomb, and J.A. Hodgeson, "A Review of Experimental Measurement Methods Based on Gas-Phase Chemiluminescence", *Chemiluminescence and Bioluminescence* M.J. Cormier, D.M. Hercules, J. Lee, Eds. (Plenum Press, New York, 1973), p. 393.
- 13 L. Pasternack and J.R. McDonald, "Reactions of $C_2(X^1\Sigma_g^+)$ Produced by Multiphoton UV Excimer Laser Photolysis", *Chem. Phys.* **43**, 173 (1979).
- 14 N. Daugey, A. Bergeat, A. Schuck, P. Caubet, and G. Dorthe, "Vibrational Distribution in $CN(X^2\Sigma^+)$ from the $N + C_2 \rightarrow CN + C$ Reaction", *Chem. Phys.* **222**, 87 (1997).
- 15 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, 1992, Chap. 6.
- 16 S.L. Baughcum and R.C. Oldenberg, "Measurement of the $C_2(a^3\Pi)$ and $C_2(X^1\Sigma)$ Disappearance Rates with O_2 from 298 to 1300 K", in *The Chemistry of Combustion Reactions. ACS Symposium Series 249*, T.M. Sloane, Ed., ACS, Washington, 1984, Chap. 15.
- 17 H. Okabe, *Photochemistry of Small Molecules*, Wiley, New York, 1978, pp. 262, 275.
- 18 A.M. Renlund, F. Shokoohi, H. Reisler, and C. Wittig, "Reactions of C_2H with O_2 : Chemiluminescent Products", *J. Phys. Chem.* **86**, 4165 (1982).
- 19 F.F. Marmo, J.P. Padur, and P. Warneck, "Vacuum Ultraviolet Chemiluminescence in the Reaction of Atomic Oxygen with Acetylene", *J. Chem. Phys.* **47**, 1438 (1967).

²⁰A. Fontijn and W. Felder "HTFFR Kinetics Studies: A Chemiluminescence Titration Method for the Determination of Absolute Sn Concentrations", Chem. Phys. Lett. 47, 380 (1977).

²¹H. Reisler, M. Mangir, and C. Wittig, "The Kinetics of Free Radicals Generated by IR Laser Photolysis. I. Reactions of $C_2(a^3\Pi_u)$ with NO, Vinyl Cyanide, and Ethylene", J. Chem. Phys. 71, 2109 (1979).

²²W.M. Pitts, L. Pasternack, and J.R. McDonald, "Temperature Dependence of the $C_2(X^1\Sigma_g^+)$ Reaction with H_2 and CH_4 and $C_2(X^1\Sigma_g^+$ and $a^3\Pi_u$ Equilibrated States) with O_2 ", Chem. Phys. 68, 417 (1982).

APPENDIX B

PROCEEDINGS OF THE NINTH
INTERNATIONAL CONFERENCE ON

HIGH TEMPERATURE MATERIALS CHEMISTRY

Editor

Karl E. Spear
The Pennsylvania State University
University Park, Pennsylvania, USA

Copyright 1997 by The Electrochemical Society, Inc.
All rights reserved.

This book has been registered with Copyright Clearance Center, Inc.
For further information, please contact the Copyright Clearance Center,
Salem, Massachusetts.

Published by:

The Electrochemical Society, Inc.
10 South Main Street
Pennington, New Jersey 08534-2896, USA

Telephone (609) 737-1902

Fax (609) 737-2743

e-mail: ecs@electrochem.org

Web site: <http://www.electrochem.org>

ISBN 1-56677-190-0

Printed in the United States of America



Sponsored by:
INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY
Inorganic Chemistry Division - Commission II.3
High Temperature Materials and Solid State Chemistry



Co-sponsored by:
THE ELECTROCHEMICAL SOCIETY
High Temperature Materials Division

Proceedings Volume 97-39

THE ELECTROCHEMICAL SOCIETY, INC.,
10 South Main St., Pennington, NJ 08534-2896

WIDE-TEMPERATURE RANGE OBSERVATIONS ON REACTIONS OF METAL ATOMS AND SMALL RADICALS

Arthur Fontjin

High-Temperature Reaction Kinetics Laboratory
The Isermann Department of Chemical Engineering
Rensselaer Polytechnic Institute
Troy, NY 12180-3590

The role of metal species in combustion processes, whether as fuels, additives, or, (often toxic) impurities is described. Optimization and control of these, and other, high-temperature processes requires understanding and knowledge of the kinetics of the individual gas-phase reactions involved, leading to meaningful models. Our experimental techniques to study the reactions in isolation from each other are discussed. The equipment used allows measurements in the approximately 300-1800 K temperature range, at pressures from 10-1000 mbar. Semi-empirical techniques have been developed to predict the temperature dependence of the rate coefficients for further reactions. Recent findings show that association and insertion reactions can play an important role in cases where abstraction was thought to be the operative mechanism.

I. INTRODUCTION

The desire to understand the dependence of chemical reaction rate coefficients and mechanisms on temperature, is to a major degree due to the necessity to control combustion processes. Metals as impurities, additives, or fuel components are present in most combustion systems, and are involved in many other high-temperature gas-phase processes. Their role can be both beneficial and detrimental. In waste incineration, power generation, and some other large scale industrial processes, they give rise to toxic emissions, whether as fine particulates or as gases.¹ The low ionization potentials of alkali metals used as additives enhances the ionization of flames, which can be used to change flame shape to prevent or enhance surface interaction, increase flame temperature, and for electrohydrodynamic and magnetohydrodynamic power generation.^{2,3} On the other hand the electron cloud resulting from the presence of alkali metals as impurities in rocket propellants hinders communication with the vehicle, but helps locating enemy missiles.⁴ However, aluminum is a major constituent of many solid rocket propellants.⁵ Hot corrosion by metal compounds formed in turbine engines is a severe problem.⁶ Combustion synthesis is increasingly being used for production of nanoscale refractory

solids of controlled narrow size distribution and high purity.⁷ For fire retardation metallic nanoparticles, formed in situ in flames, are among the most promising replacements for the environmentally unacceptable halons in current use.⁸ A preferred way for analyzing the metal content of flammable materials is analytical flame spectrometry.⁹ (Reference 9 also gives an excellent overview of the underlying physics and thermochemistry of metallic species in flames.)

With so many applications, it might be assumed that the chemistry of metals in flames is well known. However, many practical flames are diffusion flames, which do not lend themselves to fundamental physico-chemical observations because of continuous concentration gradients of fuels, oxidants, and intermediates. Many are turbulent and most are not observable from outside the devices that are powered by them, or in which they are contained. In special research burners, which are typically of the premixed flat flame type,¹⁰ a fair amount of thermochemical information on individual species and their equilibria has been obtained, particularly for charged metallic species.^{9, 11} Important as this is, flames are inherently non-equilibrium systems and their chemical characterization requires knowledge of individual reaction rate coefficients, k , as functions of temperature, T , and sometimes pressure, P . As a multitude of reactions are taking place simultaneously, reliable data on individual reactions can rarely be obtained from flames. Kinetic models with sensitivity analysis are increasingly being prepared for specific situations. In these, most rate coefficients are estimated by theoretical chemical methods. To improve the models $k(T,P)$ measurements are needed for individual reactions.

In our laboratory we have developed several reactor types for measurements on isolated combustion reactions at temperatures from 300-1800 K and pressures from about 0.01 to 1 bar. In this chapter their application to homogeneous gas-phase reactions of neutral metal atoms, metal oxides, and metal halides are discussed. In other work, one of these techniques (HTP) has also been used for reactions of O, N, H, and Cl atoms, but these are outside the scope of this presentation. The use of the reactors for study of gas-particle interactions also appears feasible, but has not yet been attempted.

The work is not restricted to metals, but includes their nearest neighbors in their periodic table groups. The reactions studied thus far include those of: Al, AlCl, AlO, BCl, BO, and BO₂ in the context of rocket propellants and advanced explosives, Cr and Cd as important toxic components from waste incinerators, Cu and CuCl because of the catalytic role of copper in forming toxic dioxins from combustion, Na which is present in most combustion systems. Earlier studies of Sn, Ge, and Ba were largely inspired by the interest in purely chemical lasers, where the high bond energies of metal oxides could be utilized. This latter work has previously been reviewed,¹² and will not be further considered here. A more recent review of some of the metal oxidation reactions has also appeared.^{13a} Most of the reactions studied have been oxidation reactions with O₂, CO₂, SO₂, N₂O, Cl₂, or HCl. However, the reaction of CH₄ with AlO has also

been investigated because of the importance of such reactions for understanding the surface phenomena of metal oxide catalysts for hydrocarbon up-conversion into the petrochemical industry. The BO_2 investigations have been reduction studies.^{6b}

While a considerable data base is thus beginning to emerge, reliable models would require significantly larger input. Practical applications can not wait until the quite time-consuming experimental work provides these. We have therefore also started to use our data base for the development of predictive techniques. The status of these semi-empirical approaches followed is also discussed in the following.

II. EXPERIMENTAL TECHNIQUES

We have developed two basic techniques for kinetic measurements over the about 300-1800 K temperature regime. These have in common that metal, or other refractory, -atoms, -oxides, or -halides are produced in small concentrations, typically 10^{10} to 10^{11} cm^{-3} , and are reacted with sufficient excess of the second, molecular, reactant to allow the measurements of the consumption of the metallic reactant to be made under pseudo first-order conditions. The concentrations of both reactants are small compared to that of the bath gas, normally Ar. This allows the pressure and temperature to be set at the desired values independently of the heat of reaction. As the concentration of the limiting reactant is small, so is that of the products. The result is that the rate of any reactant disappearance by interaction with the products is necessarily very small and usually negligible. For the rate coefficient measurements the relative concentration of the metallic species is monitored by pulsed laser-induced fluorescence, or by cw atomic absorption or fluorescence using a hollow cathode lamp. The measurable rate coefficient range is typically in the 10^{10} - $10^{15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, i.e. from reaction upon every hard-sphere collision to one in every 10^5 collisions. While the temperature range that can be covered is very wide, small reaction rates at lower temperatures, and thermal stabilities of the reactants at high temperatures, can limit the observation range for given reactions.

The reactors consist of a refractory reaction tube (alumina, mullite, or industrial grade quartz), surrounded by, in sequence, SiC resistance heating elements, Zircar insulation, and a water cooled vacuum housing. Openings in the reaction tube and insulation face the window in the housing for the spectrometric measurements. In one reactor type, the HTFFR (high-temperature fast-flow reactor), Fig. 1, the metallic reactant is produced by evaporative methods, similar to those used in thin film production techniques.¹⁴ Alternatively, we use microwave discharge flow methods through a precursor compound in bath gas Ar, e.g. BCl_3 for BCl ,^{13a} or trimethylaluminum¹⁵ for Al at low temperatures. In either case the reactant can be converted to a larger reactant by a fast reaction (e.g. $\text{Al} + \text{O}_2 \rightarrow \text{AlO} + \text{O}$).¹⁵ Immediately beyond the

source, upstream from the 20 cm observed reaction zone. This zone begins at the second reactant inlet and terminates at the level of the observation windows. Flow velocities of 10 to 150 m s^{-1} at pressures of 5 to 100 mbar are used in the 2.0-2.5 cm i.d. reaction tubes, leading to observation times in the 10⁻² to 10⁻³ s range.

The other basic type, the MHTP (metals high-temperature photochemistry) reactor, Fig. 2, operates in a pseudo-static mode. A mixture of photolyte, second reactant, and bath gas flows slowly, 5-50 cm s^{-1} , to the window plane of the wide, 5.0 cm i.d., reaction tube. A flash lamp or pulsed excimer laser is used to produce the metallic species of interest, which reacts in essentially the same volume element in which it is formed. The photolyte is typically a metal halide or carbonyl. Time scales for the measurements vary in the 10⁻⁵ to 10⁻³ s or 10⁻³ to 10⁻¹ s range depending on the generation and relative concentration measurement method used. Photolytic pulse rates are set at 1-5 Hz to provide a fresh mixture for each pulse. Total pressures are in the range of 50 to 600 mbar, but higher pressures would be accessible. As diffusion times to the walls are long compared to the observation times, MHTP operation is free of wall interference, which is an advantage over HTFFR experiments. This has, for example, allowed measurements on Na atoms,¹⁶ which were found to be reversibly absorbed by HTFFR alumina walls. When a cooled inlet¹⁷ is used in an MHTP reactor, thermally less stable second reactants can be used to higher temperatures than in an HTFFR, e.g. N_2O to about 1250 instead of 950 K, again due to the absence of wall interactions. On the other hand, a potential drawback of MHTP is that the second reactants are also in the photolysis beam and care is needed to select photolysis conditions where these are not affected. The HTFFR metal species production techniques are also more versatile.

In practice then, the two techniques well complement each other. They have several times been checked against each other and to other techniques.¹⁸ The earlier reviews,^{12,13} together with the referenced papers,¹⁵⁻¹⁸ give a more extensive description of the techniques and operational procedures than is possible here. Recently, an HTFFR has been coupled to a molecular beam mass spectrometer. This has considerably enhanced the ability to identify products and hence reaction mechanisms. The first results are discussed in Section III C.19

III. CURRENT KNOWLEDGE AND OPEN QUESTIONS

The measured rate coefficients of elementary reactions, when considered over wide temperature ranges, most frequently follow the equation

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

Here, A, n and E are constants for given reactions and R is the gas constant. In the following section, III A, we are particularly concerned with predicting the

factors that determine the temperature dependence of rate coefficients. The A coefficients can readily be estimated from classical collision theory, taking into account statistical and steric factors.²⁰ Equation (1) is an expression of the fact that Arrhenius plots, in k vs T^{-1} , are curved, though this can frequently not be seen within the accuracy of experiments. The fundamental reasons for this behavior have been discussed in several places, e.g. Ref. 21. It should be noted that E is not identical to the traditional Arrhenius activation energy E_A , which merely gives the local slope of these plots. Physically, E is the difference in the potential energy of the activated complex (transition state) and the sum of the potential energies of the reactants, i.e. it is the activation barrier.

Measured $k(T)$ values do not necessarily contain information on the products. For simple abstraction reactions these values correspond to the $k(T)$ for product formation. However, increasingly examples of other mechanisms are being encountered. These include simple pressure-dependent association reactions (Section III B), insertion reactions (Section III C), and a few²² four center reactions.

A. Comparison of Experimental Temperature Dependences to those from Semi-Empirical Theories

Figure 3 shows measurements of metallic species consumption rate coefficients in four reactions and the curves corresponding to the best fit expressions. The steeper rise of the CO_2 reactions would suggest a larger E factor than for the O_2 reactions, but since eq. (1) has two T-dependence factors such a comparison is not straightforward. It can however be achieved if it is assumed that all these reactions have, in first approximation, the same n-factor. This is reasonable as these are similar (i.e. homologous) reactions, which should have similar transition state structures. Classical transition-state theory, TST, gives

$$k(T) = \frac{k_B T}{h} \frac{q^\ddagger}{q_A q_B} \exp(-\Delta E^\ddagger/RT) \quad [2],$$

where k_B is the Boltzmann and h the Planck constant, and the q are the partition functions of the transition state (q^\ddagger) and of the reactants A and B, respectively. n is the multiplied temperature dependence of the pre-exponential terms and can in principle be found by ab initio calculations, though these can not yet be made with good reliability for most metallic species. Approximate values for n can be taken from the experimental best fit expressions. By using such values for a number of homologous reactions, plots like those of Fig. 4 are obtained, which show that the respective E values correlate with the sums of the ionization potentials IP of the metal species MeX, plus their promotion energies PE for the first allowed Σ - Π electronic transitions minus the electron affinities EA of the oxidant OY. A wide range of n values give such correlations, and allow good $k(T)$ predictions, but neither such

arbitrary n nor the corresponding E are physically meaningful. Values approximating the physically meaningful are found by taking the average difference, for the reactions of Fig. 4, between the experimental and SECI theory E values (see below) for each of a number of n values. The desired n , 1.9 in this case, is the one for which this difference is at a minimum, cf. Ref. 23. Different series of similar reactions will have different transition structures in common and require other values of n . This is shown in Fig. 5 for s^1 , s^2 , and s^2p^1 atom reactions with N_2O , for which $n = 0.5, 2.4$

SECI (Semi-Empirical Configuration Interaction Theory), is based on simple Pauling-type resonance theory and provides the physical justification for the correlation of E with IP, PE, and EA. E is found from the properties of three hypothetical resonating activated complexes, i.e. those resulting from (i) purely ground state interaction for which the barrier is q , (ii) the interaction involving the lowest excited state from an allowed s - p or Σ - Π transition of the metallic reaction partner, and (iii) ionic interaction. The wave function of the actual complex resulting from these structures is given by

$$\Psi = c_1\Psi_1 + c_2\Psi_2 + c_3\Psi_3 \quad [3],$$

where the c factors give the contributions of each structure. The actual Ψ will be that for which $E = \int \Psi^* H \Psi dt$ is at a minimum. This condition can be expressed as a set of simultaneous linear equations, ultimately resulting in

$$aq + bq^2 + cqE + dq^2E + eE + fE^2 + gE^3 = 0 \quad [4].$$

where a , b , c , d , e , f , and g , are constants derived from tabulated physical properties of the individual reaction partners. These properties are IP, PE, EA and the attractive Coulomb and repulsive Born potential, and univalent radii for the hypothetical ionic species.

E and q can not simultaneously be found from first principles. For each series, e.g. the s^1 atoms, an experimental E is used for one metallic reactant, which allows finding q for that series. This q then allows finding the E for the other reactants. As already shown in Figs. 4 and 5, good agreement is obtained between these theoretical E values and those obtained experimentally. We are currently extending the calculations to s^2p^2 atoms. Others have attempted to apply SECI to transition metal atoms and found sometimes less good agreement²⁶⁻²⁸ than for the main group atoms. This will be investigated further. There is no a priori reason to consider only three resonating states. Quite likely, interactions involving d electrons have to be considered for transition elements.

In other semi-empirical theoretical work, for which the present format leaves no room, we have shown that, for abstraction reactions, a modified form

of TST allows predicting the shape of an Arrhenius plot from a measurement at one temperature.^{29,30}

B. Association Reactions

Association reactions of metallic species have frequently been observed, e.g. oxidation reactions of alkali and alkaline earth atoms.^{13b,16} Most of these have negative temperature dependences and their potential contribution at high temperatures has tended to be neglected. An example of this is the Cr/O₂/M system (M = third body), which is important for the formation of highly carcinogenic hexavalent chromium in incinerators. There were reports in the literature that near room temperature the reaction proceeded by association



whereas above about 800 K the mechanism would be abstraction



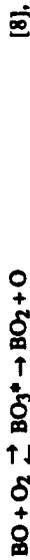
Below that temperature in an MHTP study, we only found evidence for reaction (5) and above it, reaction (6) indeed proceeded at a measurable rate, but was initially not dominant. The measurements showed that even at 1500 K and 1 bar, upper limits for incinerator conditions, reaction (6) is only some 1.4 times faster than (5).¹⁸ The problem was that in the original T > 800 K study the pressure had not been varied. It has yet to be established if (5) and (6) are independent reactions or proceed through a common CrO₂ intermediate, the dissociation of which becomes more significant with increasing temperature.

Another example here is the AlO/O₂/M system. In an early HTFFR study, with considerable data scatter, no pressure dependence had been found which led to the erroneous interpretation of a complex abstraction reaction with a negative T-dependence. Later HTFFR work, following many apparatus improvements, showed an association reaction to dominate to about 1000 K for which $k(T) = -25.36 - 1.69 \log(T/K) \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1}$, while above that temperature a second order process was also observed with $k(T) = 7.7 \times 10^{-10} \exp(-10008 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁵ The likely reaction mechanism is, like for the preceding example, a competition between collisionally stabilized association and dissociation



There have not been any direct gas-phase observations of AlO₃, but the species has been observed in matrix work.³¹ By contrast, the O₂ reaction of the "iso-electronic" species BO has been found to be pressure independent over the 300-

960 K range, where it shows a negative T-dependence: $k(T) = 7.9 \times 10^{-12} \exp(161 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^{8b} The mechanism proposed here is³²



where the smaller pre-exponential of $k(T)$, as compared to that for AlO₂ + O formation, indicates a preferential dissociation of the intermediate to the reactants. Ab initio calculations have suggested a branched ring OBO₂ structure for BO₃,³² similar to that indicated for AlO₃ in the matrix study.

C. Insertion Reactions

There have been frequent experimental and theoretical studies of metal atoms inserting into molecular bonds.³³ Most of the experiments have been conducted at room temperature and below. Similar reactions involving gaseous metal oxides would also be of interest, as these would be representative of processes occurring on metal oxide catalysts. In this context, an ab initio study has predicted that AlO can directly abstract an H atom from methane in an exothermic reaction with a considerable barrier, 67 kJ mol⁻¹.³⁴ However, an HTFFR investigation over the 590-1350 K range showed much lower activation energies except at the highest temperatures; the complex expression, required to fit the data, indicated competition between several paths.³⁵ Further calculations suggest that direct abstraction can indeed occur, but that insertion leading to CH₃AlOH is the most likely initial attack step.³⁵

A more direct example of a high temperature insertion reaction was obtained for Cu + HCl.¹⁹ No pressure dependence was observed and a simple Arrhenius plot with $k(680-1500 \text{ K}) = 1.2 \times 10^{-10} \exp(-7719 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained, suggesting an abstraction reaction. However, mass spectrometric observations over the approximate 1150-1500 K range showed, in addition to the product CuCl, a species HCuCl, the formation of which would require a third-body collision. Ab initio calculations indicated that the initial reaction proceeds over a common rate-controlling barrier, after which the HCuCl complex can either be stabilized into a potential well, or dissociate to H + CuCl. This suggested that increasing pressure would favor the branching to HCuCl, while increasing temperature would decrease its relative importance. This was borne out by experiment.

These observations lead to the questions how common such reactions are and whether other reactions, that on the basis of rate coefficient observations have been assumed to proceed by abstraction, are in fact more complex. In our further work we hope to start providing answers. Hranisvljevic has suggested the use of some orbital symmetry rules and electron configuration arguments to help predict when to expect insertion.^{36,37} We plan to start testing these shortly.

IV. CONCLUDING REMARKS

In this brief review the emphasis has been placed on the temperature dependence of metallic species reactions, particularly with a view toward high-temperature observations. The study of gas-phase metallic species reactions per se had not been of major interest to kineticists. A 1992 edited volume¹³ had already shown that this is changing, with most work being done well below 1000 K. Since then several other investigators have joined and we may, as a result, expect rapid advances. However, a disturbing trend, fortunately restricted to few investigators, must be noted. That is, work done only at one pressure or one [M]. The discussion of Section III B shows that this can readily lead to erroneous interpretations. Likewise, I urge my colleagues to use as wide a temperature range as their experiments allow, when determining activation energies or barriers; such data from narrow T-1 ranges can not be very reliable.

ACKNOWLEDGEMENT

I thank my collaborators whose names appear in the references. Over the years this work has been supported by various U.S. Government Agencies, currently these are NSF, AFOSR, and ONR.

REFERENCES

- (1) D.A. Tillman. *Trace Metals in Combustion Systems*, Academic Press, San Diego, 1994.
- (2) J. Lawton and F.J. Weinberg. *Electrical Aspects of Combustion*, Clarendon Press, London (1969).
- (3) F.J. Weinberg, Ed. *Advanced Combustion Methods*, Chap. 5 (F.J. Weinberg) and Chap. 6 (D. Bradley), Academic Press, London (1986).
- (4) H.S. Pergament and H.F. Calcoete. In *Eleventh Symposium (International) on Combustion*, p. 597, The Combustion Institute, Pittsburgh (1967).
- (5) Y.M. Tinmat, *Advanced Chemical Rocket Propulsion*, Academic Press, London (1987).
- (6) J.W. Hastie. *High Temperature Vapors, Science and Technology*, Section II.4, Academic Press, New York (1975).
- (7) K. Brezinsky. In *Twenty-Sixth Symposium (International) on Combustion*, p. 1805, The Combustion Institute, Pittsburgh (1996).
- (8) 1996 Fall Technical Meeting, The Eastern States Section of the Combustion Institute, The Combustion Institute, Pittsburgh. a) V. Babushok, W. Tsang, G.T. Linteris, and D. Reinelt, p. 265. b) D.P. Belyung, G.T. Dalakos, Q. Zhang, J.-D.R. Rocha, and A. Fontijn, p. 503.
- (9) C.Th.J. Alkemade, Tj. Hollander, W. Snelleman, and P.J. Th. Zeegers. *Metal Vapors in Flames*, Pergamon Press, Oxford, 1982.
- (10) Ref. 3, pp. 66-70.

- (11) W.J. Miller. In *Fourteenth Symposium (International) on Combustion*, p. 307, The Combustion Institute, Pittsburgh (1973).
- (12) A. Fontijn and W. Felder. In *Reactive Intermediate in the Gas Phase, Generation and Monitoring*, (D.W. Setser, ed.), Chap. 2, Academic Press, New York (1979).
- (13) A. Fontijn, Ed., *Gas-Phase Metal Reactions*, North-Holland, Amsterdam (1992).
- (14) a) A. Fontijn and P.M. Futerko, Chap. 6. b) J.M.C. Plane, Chap. 3. R. Glang. In *Handbook of Thin Film Technology* (L.I. Maissel and R. Glang, Eds.), Chap. 1, McGraw Hill, New York (1970).
- (15) D.P. Belyung and A. Fontijn. *J. Phys. Chem.* **99**, 12225 (1995).
- (16) P. Marshall, A.S. Narayan, and A. Fontijn. *J. Phys. Chem.* **94**, 2998 (1990).
- (17) A.S. Narayan, P.M. Futerko, and A. Fontijn. *J. Phys. Chem.* **96**, 290 (1992).
- (18) A. Fontijn, A.S. Blue, A.S. Narayan, and P.N. Bajaj. *Combust. Sci. and Tech.*, **101**, 59 (1994).
- (19) D.P. Belyung, J. Hranisavljevic, O.E. Kashireminov, G.M. Santana, A. Fontijn, and P. Marshall. *J. Phys. Chem.*, **100**, 17835 (1996).
- (20) P.M. Futerko and A. Fontijn. *J. Chem. Phys.*, **98**, 7004 (1993).
- (21) A. Fontijn and R. Zellner. In *Reactions of Small Transient Species. Kinetics and Energetics*, (A. Fontijn and M.A.A. Clyne, Eds.) Chap. 1, Academic Press, London (1983).
- (22) J.A. Silver and C.E. Kolb. *J. Phys. Chem.*, **90**, 3267 (1986).
- (23) A.S. Blue, D.P. Belyung, and A. Fontijn. *J. Chem. Phys.*, submitted.
- (24) D.P. Belyung, P.M. Futerko, and A. Fontijn. *J. Chem. Phys.*, **102**, 155 (1995).
- (25) P.M. Futerko and A. Fontijn. *J. Chem. Phys.*, **95**, 8065 (1991).
- (26) J.M.C. Plane and R.J. Rollason. *J.C.S. Faraday Trans.*, **92**, 4371 (1996).
- (27) M.L. Campbell. *J. Phys. Chem.*, **100**, 19430 (1996).
- (28) R. Matsui, K. Senba, and K. Honma. *J. Phys. Chem.*, **A101**, 179 (1997).
- (29) P.M. Futerko and A. Fontijn. *J. Phys. Chem.*, **97**, 7222 (1993).
- (30) P.M. Futerko, A.G. Slavejkov, and A. Fontijn. *J. Phys. Chem.*, **97**, 11950 (1993).
- (31) L. Andrews, T.R. Burkholder, and J.T. Yustein. *J. Phys. Chem.*, **96**, 10182 (1992).
- (32) C.T. Stanton, N.L. Garland, and H.H. Nelson. *J. Phys. Chem.*, **95**, 8741 (1991).
- (33) S. Sakai. *J. Phys. Chem.*, **96**, 8369 (1992).
- (34) K.J. Borve and L.G.M. Pettersen. *J. Phys. Chem.*, **95**, 3214 (1991).
- (35) D.P. Belyung, A. Fontijn, and P. Marshall. *J. Phys. Chem.*, **97**, 3456 (1993).
- (36) J. Hranisavljevic, Ph.D. Thesis, Rensselaer Polytechnic Institute, (1997).
- (37) J. Hranisavljevic and A. Fontijn. *J. Phys. Chem.*, **101**, 2323 (1997).

