$C_2 Br_2 F_4$ Plasma Quench Investigations

J. M. Madson,* J. H. Mullen,†
and L. N. Medgyesi-Mitschang*
McDonnell Douglas Corporation, St. Louis, Mo.

Introduction

THE reaction processes which govern the production and loss of electrons together with reactions between ionized and neutral molecules play an important role in determining the plasma environment of a vehicle during atmospheric re-entry. Since the ability to detect a vehicle electronically during this portion of the trajectory is influenced by the interaction of propagating electromagnetic waves with electrons in the plasma, it is desirable to predict the composition of the plasma, particularly the plasma electron density, and modify and/or control it. To describe the environmental conditions of re-entering vehicles, aerothermochemical models have been developed. These models predict the electron density around a vehicle as a function of vehicle geometry and flight environment.[1-3]

When electrophilic molecules are injected into a re-entry plasma environment, electron removal (plasma quench) occurs through the process of electron attachment to an electrophilic molecule forming a negative ion.[4] The reaction rate constants for the dominant quench processes are needed as input data in the aerothermochemical models to predict the change in electron density resulting from the quench reactions.

In the past, many of the data relating to high-temperature electron attachment reactions were obtained by extrapolating room-temperature data to re-entry temperatures. However, experience has shown that electron attachment reaction rate constants for certain electrophilic molecules are strongly temperature dependent,[5,6] thus making this approach unacceptable.

In addition to the need for information regarding the quench effectiveness (as indicated by the attachment rate constant) of electrophilic agents as input data for aerothermochemical models, these data also are needed for the design and development of onboard deployment techniques for injecting the agents into the vehicle boundary layer or wake.[7] This Note describes the results of a series of measurements on the attachment properties of dibromotetrafluoroethane, $C_2Br_2F_4$ (Freon 114B2), from 1430 to 2650 K.

Experimental System

Experimental evaluation of the quench effectiveness of electrophilic compounds was performed within the McDonnell Douglas Research Laboratories (MDRL) Plasma Chemistry Facility (PCF). The experimental system and associated diagnostic instrumentation have been described in detail elsewhere[8-10]; only a brief description will be given here.

The PCF provides a steady-state, flowing plasma environment for high-temperature reaction chemistry. Electrophilic quenchant molecules are injected into the reaction chamber in the gas phase and rapidly acquire the temperature of the argon gas in the chamber through collisional heating. The quenchant molecules react with the flowing argon plasma for a time equivalent to the transit time through the chamber. The transit time is determined by the chamber length and the argon gas temperature and is normally of the order of 10 μsec.

The flowing plasma, injected quenchant, and quenchant-plasma reaction products undergo a freejet expansion after leaving the reaction chamber. The rapid expansion sharply decreases the interparticle collision frequency and thereby reduces the rate of chemical reaction. The expansion flowfield for a freejet is well known and has been described (see for example Knuth,[11] French,[12] and references therein). The expansion preserves the reaction products formed in the reaction chamber for sampling and analysis.

A molecular beam is formed by sampling the centerline flow of the freejet expansion with a conical extractor. The beam contains both electrically charged and neutral constituents of the discharge chamber plasma as well as reaction products from the reaction chamber. A conical skimmer placed in the high-vacuum chamber behind the extractor further defines the beam geometry. After passing through the skimmer, the beam is modulated by a 435-Hz tuning fork chopper. The modulated beam enters the ionizer assembly where it is focused onto the entrance of a quadrupole mass spectrometer (Extranuclear Laboratories, 0 to 1010 amu). When the beam is electrically neutral, the ionizer filament is energized to produce a representative sample of ions for mass analysis. The mass-analyzed positive or negative ions are detected by a continuous dynode channeltron multiplier. When ions created in the plasma source or reaction chamber are analyzed, beam modulation and phase-sensitive detection increase the signal-to-noise ratio by eliminating dc background signals caused by radiation striking the multiplier. When ions are created in the ionizer, beam modulation makes it possible to separate signals which are caused by ambient background gas from those which arise from the beam gas.

Plasma Quench Measurements

A measure of the overall quench effectiveness of a given electrophile can be obtained by measuring the decrease in plasma electron density resulting from the addition of the electrophile. Electron attachment rate constants for a specific reaction, however, must be obtained from mass-analyzed negative-ion current variation as a function of quenchant concentration together with the electron and quenchant number densities in the reaction chamber. The decrease in electron density with quenchant concentration, measured by the microwave interferometer, gives an indication of the total quench effect which may be a result of several negative-ion forming processes occurring simultaneously. In the event that a single negative-ion forming reaction is the only electron loss process, the attachment rate constant can be obtained from the slope of the electron density curve.

The electron attachment properties of dibromotetrafluoroethane, $C_2Br_2F_4$ (Freon 114B2), from 1430 to 2650 K were determined because of interest in this compound as a quenchant for onboard deployment during atmospheric re-entry.[13,14] The mass-analyzed negative-ion current resulting from electron attachment reactions between the injected $C_2Br_2F_4$ and the argon plasma was measured as a function of the $C_2Br_2F_4$ concentration (mole % in argon). In all cases with $C_2Br_2F_4$, F^- was the dominant negative ion. An example of the mass-analysed F^- ion current as a function of $C_2Br_2F_4$ concentration in argon is shown in Fig. 1. These data were obtained without beam modulation and phase-sensitive detection.

The chemical composition of the argon-$C_2Br_2F_4$ mixtures as a function of temperature was calculated by assuming thermodynamic equilibrium. The calculations were made using an equilibrium thermochemical computer program which minimizes the Gibb's free energy of the system for each temperature and pressure. The calculations indicate that, if thermodynamic equilibrium exists in the reaction chamber,

Received Jan. 14, 1977; presented as Paper 77-110 at the AIAA 15th Aerospace Sciences Meeting, Los Angeles, Calif., Jan. 24-26, 1977; revision received April 5, 1977.

Index categories: Thermochemistry and Chemical Kinetics; Atmospheric and Space Sciences.

*Scientist, Research Laboratories. Member AIAA.

†Senior Scientist, Research Laboratories.

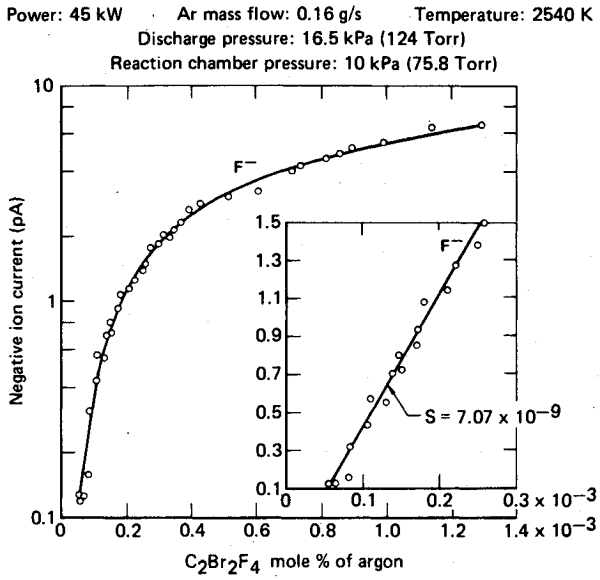

Fig. 1 Negative ion current vs $C_2Br_2F_4$ concentration in argon.

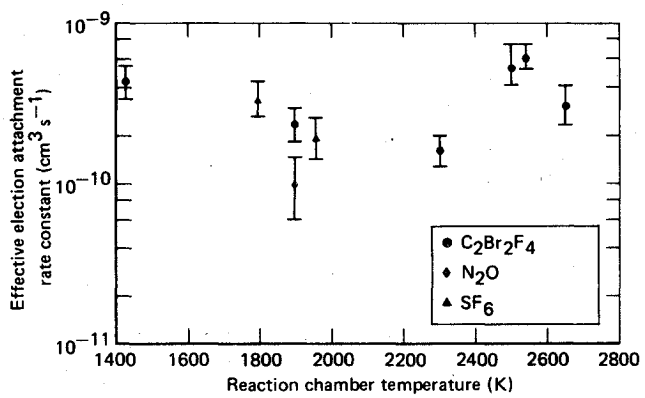

Fig. 2 Electron attachment rate constants.

the major electrophilic species are F, Br, and CF_2. However, in our experimental apparatus, the $C_2Br_2F_4$ vapor is supersonically injected into a plasma flowing at sonic velocity through a cylindrical reaction chamber; thus, the $C_2Br_2F_4$ vapor passes through a temperature gradient while moving from the chamber wall to the centerline. Under these conditions, thermodynamic equilibrium is not attained, and our experimental observations indicate less decomposition than predicted theoretically.

Considering the equilibrium calculations together with the fact that F^- was the dominant negative ion detected in the experiment, it appears that F^- is formed by a dissociative attachment process involving a thermal decomposition fragment, such as CF_2, or by a three-body attachment process with free fluorine atoms. These reactions are illustrated in Eqs. (1) and (2), respectively:

$$e + CF_2 \rightarrow F^- + CF \quad (1)$$

$$e + F + M \rightarrow F^- + M \quad (2)$$

where M is a third body. Reaction (1) appears more probable since $D(CF-F) = 4.48$ eV (dissociation energy) and $EA(F) = 3.62$ eV (electron affinity) leaving an energy difference $\Delta E = 0.86$ eV. This endothermicity can be supplied by the initial energy of the electrons. In addition, if the CF_2 were vibrationally excited, the reaction would be enhanced. For reaction (2) to occur, the third body (in this reaction argon is the most probable candidate) would have to absorb the excess energy of the reaction which is at least equal to the electron affinity of the fluorine atom. Since this energy must be carried away as an increase in kinetic energy of the argon atom, reaction (2) appears improbable. In addition, the rate constants for the three-body attachment process are much smaller than those determined in this investigation.[15,16] Although the equilibrium calculation indicates Br to be one of the dominant decomposition products, only a trace amount of Br^- was detected. The absence of Br^- is further evidence of the small rate constant for three-body attachment for the conditions of this experiment.

Assuming that a two-body reaction of type (1) occurs, we can determine the effective electron attachment rate constants. These calculations were made using the initial slope of the ion intensity data (see insert in Fig. 1), the electron and $C_2Br_2F_4$ vapor number densities in the reaction chamber, and the reaction time. The electron density is measured with a microwave interferometer, and the $C_2Br_2F_4$ vapor number density is calculated from calibrated injection orifice flow properties. The reaction time is obtained from the gas flow velocity through the reaction chamber. The rate constants are summarized in Fig. 2 with error bars indicating the estimated accuracy. For comparison, the rates of attachment to form O^- from N_2O and F^- from SF_6 also are shown. Over the temperature range investigated and within the experimental accuracy of the measurements, the rate constants are independent of temperature from 1430 to 2650 K.

Summary

An experimental facility for studying high-temperature plasma quench reactions under conditions which simulate reentry and wake environments in terms of temperature, pressure, and plasma electron density has been used to investigate the quench effectiveness of $C_2Br_2F_4$. Electron attachment measurements in $C_2Br_2F_4$ from 1430 to 2650 K show that this compound is an effective quenchant producing negative fluorine ions (F^-) as the major product of the quench reactions. The reaction rate for the formation of F^- is nearly constant with an average value of $3.7 \times 10^{-10} cm^3 s^{-1}$ over the foregoing temperature range.

Acknowledgments

We wish to express our thanks to R.A. Hefferlin for his assistance in the spectrographic measurements and his technical advice on the plasma source and reaction chamber conditions. We are also indebted to E.A. Theby for his assistance in the mechanical design, construction, and operation of the PCF. This research was sponsored in part by Air Force Cambridge Research Laboratories, Air Force Systems Command, under Contract F196-71-C-0024 and by McDonnell Douglas Independent Research and Development Program.

References

[1] Lew, H.G., "The Ionized Flow Field Over Re-entry Bodies," General Electric TR R67SD70, 1967.

[2] Lew, H.G., "A Study of Electron Density Distribution in Viscous Flows," Air Force Cambridge Research Laboratories, AFCRL-72-0718, Nov. 1972.

[3] Schexnayder, C.J., Jr., Huber, P.W., and Evans, J.S., "Calculation of Electron Concentration for a Blunt Body at Orbital Speeds and Comparison with Experimental Data," NASA TN D-6294, 1971.

[4] Pergament, H.S. and Kau, C., "A Computer Code to Predict the Effects of Electrophilic Liquid Injection on Re-entry Plasma Sheath Properties," Air Force Cambridge Research Laboratories, AFCRL-TR-74-0074, Jan. 1974.

[5] Henderson, W.R., Fite, W.L., and Brackman, R.T., "Dissociative Attachment of Electrons to Hot Oxygen," *Physical Review*, Vol. 183, July 1969, pp. 157-166.

[6] Chantry, P.J., "Temperature Dependence of Dissociative Attachment in N_2O," *Journal of Chemical Physics*, Vol. 51, Oct. 1969, pp. 3369-3379.

[7]Lennon, J.F. and Herskovitz, S.B., "Design and Testing of a Chemical Injection System for Re-entry Plasma Alleviations," Air Force Cambridge Research Laboratories, AFCRL-TR-74-0113, Feb. 1974.

[8]Madson, J.M., Mullen, J.H., and Medgyesi-Mitschang, L.N., "High Temperature Plasma Quench Investigation," AIAA Paper 77-110, 1977, Los Angeles, Calif.

[9]Mullen, J.H., Madson, J.M., Medgyesi-Mitschang, L.N., Peng, T.C., and Doane, P.M., "Apparatus for the Measurement of High-Temperature Reactions," *Review of Scientific Instruments*, Vol. 41, Dec. 1970, pp. 1746-1754.

[10]Medgyesi-Mitschang, L.N. and Hefferlin, R.A., "Characteristics of an Argon rf Plasma: Active Discharge and Laminar Sonic Flow Region," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 12, 1972, pp. 1627-1639.

[11]Knuth, E.L., "Supersonic Molecular Beams," *Applied Mechanics Review*, Vol. 17, Oct. 1964, pp. 751-762.

[12]French, J.B., "Continuum Source Molecular Beams," *AIAA Journal*, Vol. 3, June 1965, pp. 993-1000.

[13]Mullen, J.H., Madson, J.M., and Medgyesi-Mitschang, L.N., "An Experimental Investigation of Electron Attachment in a High Temperature Plasma," Air Force Cambridge Research Laboratories, AFCRL-TR-0208, MDC Q0494, May 1973.

[14]Hayes, D.T., Herskovitz, S.B., Lennon, J.F., and Poirer, J.L., "Flight Test Data Comparing Electron Attachment by Ablation Products and by Liquid Injection," AIAA Paper 73-692, 1973, Palm Springs, Calif.

[14]Modica, A.P., "Microwave Measurements of Nonequilibrium Air Plasmas Behind Shock Waves Containing Electrophilic Gases," *Journal of Physical Chemistry*, Vol. 71, Oct. 1967, pp. 3463-3469.

[16]Good, R.E., "Electron Attachment to Atomic Fluorine in Thermally Ionized Air," NASA CR-516, July 1966.

Expansion Tunnel Performance with and without an Electromagnetically Opened Tertiary Diaphragm

Charles G. Miller*
NASA Langley Research Center, Hampton, Va.

Introduction

PREDICTIONS[1] for expansion tunnel flow demonstrate that substantial losses in available test time occur when the nozzle is not evacuated to a much lower initial pressure than the quiescent acceleration gas. To obtain a lower initial nozzle pressure, a diaphragm must be used to separate the acceleration section and nozzle. This diaphragm, referred to as the tertiary diaphragm,[2] must be self-opened, since experiment has shown a flow-ruptured diaphragm results in a degradation in nozzle entrance flow quality.[2] Naturally, such a diaphragm cannot open instantaneously as assumed in prediction,[1] and because of the finite opening time, the opening must be synchronized with the flow arrival at the diaphragm. Upon opening the tertiary diaphragm, an expansion wave propagates into the quiescent acceleration gas at the ambient speed of sound. If the diaphragm is opened too soon in the flow sequence, the flow will experience a density gradient in the acceleration gas in the vicinity of the nozzle entrance. The time available for the spreading of this density gradient is reduced if the opening is initiated at the proper time. If the flow arrives prior to removal of the diaphragm from the nozzle entrance, a reflected shock will be produced,[3] resulting in a degradation of nozzle flow quality.

Received Jan. 26, 1977; revision received April 5, 1977.

Index categories: Nozzle and Channel Flow; Supersonic and Hypersonic Flow.

*Aerospace Engineer, Entry Gas Dynamics Group, Aerothermodynamics Branch, Space Systems Division. Member AIAA.

The purposes of the present study are to 1) examine the effect of synchronization of an electromagnetically opened tertiary diaphragm with flow arrival at the diaphragm on the pitot pressure measured at the test section of the Langley expansion tunnel and 2) determine the effect of tertiary diaphragm pressure ratio (ratio of initial nozzle pressure to quiescent acceleration section pressure) on the pitot pressure time history. As a point of interest, the present study revealed the inadequacy of a pressure transducer protection arrangement used in previous expansion tube and expansion tunnel tests.[3] This inadequacy, in terms of response time, is demonstrated herein for the short test time of the expansion tunnel and low magnitude of pitot pressure.

Apparatus and Tests

The Langley expansion tube[4] is basically a 15.24-cm-diam tube divided into three sections by two diaphragms; thus, this facility may be viewed as a shock tube with a constant diameter tube section added to the downstream end. The driver gas is introduced into the upstream, high-pressure section and the intermediate section is filled with the desired test gas. The downstream section is referred to as the expansion or acceleration section and is filled with the acceleration gas. Thick steel diaphragms separate the driver and intermediate sections, whereas a thin Mylar diaphragm separates the intermediate and acceleration sections. The expansion tunnel[3] is simply an expansion tube with a nozzle installed at the exit of the acceleration section. A third or tertiary diaphragm separates the acceleration section and nozzle so that the initial nozzle pressure may be lower than the quiescent acceleration gas pressure.

The idealized operating sequence of the expansion tube is shown schematically in Fig. 1. Upon rupture of the primary diaphragm, an incident shock propagates through the test gas and encounters and ruptures the low-pressure secondary diaphragm. A secondary incident shock propagates into the acceleration gas and the shock-heated test gas undergoes an isentropic, unsteady expansion as it passes through the upstream expansion wave generated upon rupture of the secondary diaphragm. This expansion process generates hypersonic and hypervelocity flow at the acceleration section exit from the low Mach number shock-tube flow which encounters the secondary diaphragm. For the expansion tunnel, the test gas undergoes an isentropic steady expansion in the nozzle following removal of the tertiary diaphragm at the acceleration section exit.

An electromagnetically opened tertiary diaphragm[2] was employed. The concept is to use electromagnetic repulsive forces in a wire to rip open a Mylar diaphragm and rapidly withdraw the Mylar from the flow path. In this study, the copper wire was 13 AWG (American Wire Gage), the Mylar was 12.7 μm thick, and the energy storage system (which consisted of two capacitors, each rated at 5 kV and 100 μf) was charged to 3.2 kV. This voltage produced opening times[2] of 700 to 900 μsec without wire breakage. The tertiary

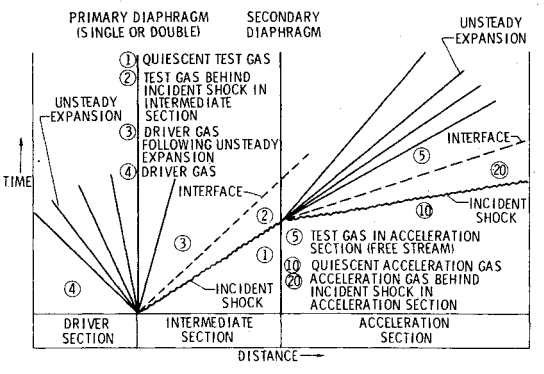

Fig. 1 Schematic diagram of expansion tube flow sequence.