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AFOSR—TR-71-2481

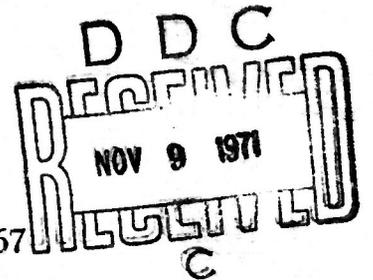
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ABSTRACTS OF PAPERS  
12th AFOSR CONTRACTORS' MEETING  
ON  
KINETICS OF ENERGY CONVERSION

September 9-10, 1971



Grant No. AF-AFOSR—1291-67



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Kalamazoo, Michigan

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13. ABSTRACT  
This report is a compilation of abstracts of the research results presented at the 12th AFOSR Contractors Meeting on Kinetics of Energy Conversion held at Western Michigan University in Kalamazoo, Michigan on 9-10 September 1971. The research presented was concerned with the topics of combustion and ignition kinetics, rates of elementary reactions, and the preparation of and the study of the properties of energetic species.

AFOSR Scientific Report

AFOSR-TR-71-2481

Abstracts of Papers

12 TH AFOSR CONTRACTORS MEETING

on

KINETICS OF ENERGY CONVERSION

9 September, 1971

Prepared by  
Thomas Houser

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12TH AFOSR CONTRACTORS' MEETING  
on  
KINETICS OF ENERGY CONVERSION

9-10 SEPTEMBER 1971  
WESTERN MICHIGAN UNIVERSITY

AGENDA

Thursday - 9 September 1971

0900	REGISTRATION	
0920	Welcome - Host	
0930	Welcome - AFOSR	
0940	Oxidation Reaction Studies of the Paraffin Hydrocarbons	L. Glassman Princeton University
1010	Absolute Rate Constants For Combustion Reaction Involving Free Radicals	D. Golden Stanford Research Institute
1040	COFFEE BREAK	
1100	Reactions of HO <sub>2</sub> Radicals with Hydrocarbons	R. W. Walker Hull University
1130	Nonequilibrium Combustion Products	R. F. Sawyer University of California (Berkeley)
1200	Ignition of Simple Alkanes in Shock Waves	K. Scheller Wright-Patterson A. F. B.
1230	LUNCH	
1345	Spectroscopy of Selected Diatomic Metal and Metal- Oxide Molecules	H. P. Broida University of California (Santa Barbara)
1415	Energy Transfer Processes In Gas Laser Materials	D. J. Seery United Aircraft Research Labs.

AGENDA

Thursday - 9 September 1971

- |      |   |   |
|------|---|---|
| 1445 | Vibrational Excitation of Deuterium Fluoride and Hydrogen Fluoride by Atomic and Diatomic Species | W.C. Solomon<br>Edwards RPL                       |
| 1515 | COFFEE BREAK  |   |
| 1530 | Studies of Excited Hydrogen in Relation to Advanced Propulsion                                    | J.M. Flournoy<br>Tetra Tech.                      |
| 1600 | Kinetic Cross Sections for Electron, Atom and Molecule Collisions                                 | H.H. Michels<br>United Aircraft<br>Research Labs. |
| 1630 | Molecular Energy from a Crossed Beam Experiment   | E.W. Rothe<br>Wayne State<br>University           |
| 1930 | DINNER  |   |

Friday - 10 September 1971

- |      |   |  |
|------|---|--|
| 0900 | Combustion Kinetics of Tetrafluoroethylene  | R.A. Matula<br>Drexel University   |
| 0930 | Equilibrium Constants for the System, Bistrifluoromethyl Peroxide, Carbonyl Fluoride, Trifluoromethyl Hypofluorite. | J.E. Levy<br>George Washington<br>University                                     |
| 1000 | Studies of Reactions of Fluorine Containing Compounds   | H.J. Schumacher<br>Consejo Nacional<br>de Investigaciones<br>La Plata, Argentina |
| 1030 | COFFEE BREAK  |  |
| 1050 | Chemical Kinetics of Fluorine Combustion Systems  | D.I. MacLean<br>Boston College   |
| 1120 | Decomposition Kinetics of the Rocket Oxidizer Ammonium Perchlorate  | E.E. Peterson<br>University of<br>California<br>(Berkeley)                       |

AGENDA

Friday - 10 September 1971

1150	The Use of $O^{17}$ in Studying the Properties and Chemistry of Various Oxidizers	I. J. Solomon IIT Research Institute
1220	LUNCH	
1330	Photochemistry of Inter-halogens	K. H. Mueller Rocketdyne Division of North American Rockwell
1400	Rates and Mechanisms of Reactions of Fluorine Containing Rocket Propellants	T. Houser Western Michi- gan University
1430	Interfacial Chemical Reactions	D. E. Rosner Yale University
1500	COFFEE BREAK	
1515	Properties of Energetic Ions Trapped in Solids: Drift Mobilities of Photoexcited Electrons in Glassy Matrices	L. Kevan Wayne State University
1545	Energy Migration in Irradiated Solids	J. Cunningham University College of Cork, Cork Ireland
1615	Production and Molecular Energetics of High Energy Rocket Propellant Ingredients Using Cryochemical Engineering Techniques	H. A. McGee, Jr. VPI and State University

## OXIDATION REACTION STUDIES OF THE PARAFFIN HYDROCARBONS\*

F. Dryer, D. Naegeli and I. Glassman

Guggenheim Laboratories

Princeton University

Princeton, New Jersey

The objectives of the program are (1) measurement of the high temperature oxidation reactions of paraffin hydrocarbon fuels in a turbulent flow reactor, (2) development of appropriate global rate expressions to characterize these reactions, and (3) better physical understanding of the elementary chemical kinetics. Development of spatial chemical sampling, analysis and data reduction techniques for use with a turbulent flow reactor have been completed. Spatial chemical measurements on the high temperature reaction of methane in oxygen-rich atmospheres have established that the global rate expression proposed in earlier work [1] is correct. The rate of disappearance of methane has been conclusively shown to be independent of water concentration, in contrast to the work of Hottel, et al. [2]. Oxidation paths to carbon dioxide other than through carbon monoxide are not necessary for explanation of the observed rate of formation of carbon dioxide, and elementary reactions of methane with radical species other than OH appear important in determining the rate of disappearance of methane.

Experiments on the associated oxidation of carbon monoxide in moist atmospheres also have been conducted. The overall rate of oxidation in oxygen-rich environments is first order in carbon monoxide and exhibits fractional orders of approximately .5 and .25 for water and oxygen concentrations. For  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$  to be the rate determining step in the reaction mechanism, OH concentrations must be some 200-300 times greater than their equilibrium value. Theoretical work using simple transition state theory suggests that the reaction  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$  has a notable pre-exponential temperature dependence and that previous measurements of the elementary rate constant at high temperatures may be more accurate than presently is recognized.

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\* AFOSR GRANT No. 69-1649

1. "Overall Reaction Rates of Paraffin Hydrocarbons" by F. Dryer and I. Glassman, 10th AFOSR Contractors' Meeting on Chemical Kinetics of Propulsion, University of California, Berkeley, Calif., 1969.
2. "The Combustion of Methane on a Jet Mixed Reactor", G.C. Williams, H.C. Hottel, and A.C. Morgan, 12th Symposium (International) on Combustion, The Combustion Institute, pp. 913 (1969).

ABSOLUTE RATE CONSTANTS FOR COMBUSTION REACTION  
INVOLVING FREE RADICALS

David M. Golden, Michael Perona,<sup>\*</sup>

John I. Brauman,<sup>\*\*</sup> and Sidney W. Benson

Department of Thermochemistry and Chemical Kinetics  
Stanford Research Institute, Menlo Park, California 94025

This report concerns work carried out under contract NAE-71-054-N from 1 June to 1 September 1971.

We have obtained preliminary data on the values of the rate constants for the recombination and disproportionation of t-butyl radicals, as well as the rate constant for the reaction of t-butyl with HI. Also, we have data on the same reactions of ethyl radicals.

Using 2,2'-azoisobutane ( $\text{t-C}_4\text{H}_9\text{-N=N-t-C}_4\text{H}_9$ ) as a thermal source of t-butyl radicals in a VLPP reactor, we have observed the formation of nitrogen, isobutane, isobutylene, and neooctane ( $\text{t-C}_4\text{H}_9\text{-t-C}_4\text{H}_9$ ) mass spectrometrically. Because reactions in the stirred flow Knudsen cell reactor of VLPP must effectively compete with escape through the exit aperture, rate constants may be evaluated relative to the "rate constant" for escape which is calculable from knowledge of the radius of the aperture and the volume of the reactor.

The same sort of data can be collected for ethyl radicals using either ditertiary amyl peroxide (dtap) ( $\text{t-amyl-O-O-t-amyl}$ ) as a source of  $\text{C}_2\text{H}_5$  radicals ( $\text{dtap} \rightarrow 2 \text{ t-amyl-O} \rightarrow 2\text{C}_2\text{H}_5 + 2 \text{ Acetone}$ ) or dipropionyl peroxide  $[(\text{C}_2\text{H}_5\text{-C}(=\text{O})\text{O})_2 \rightarrow 2 \text{ C}_2\text{H}_5\text{-C}(=\text{O})\text{O} \rightarrow 2 \text{ C}_2\text{H}_5 + 2 \text{ CO}_2]$ .

At this early stage of the work there are some problems, possibly attributable to heterogeneous effects or "hot radical" effects. Experiments are currently under way to clarify these points.

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<sup>\*</sup> Postdoctoral Research Associate

<sup>\*\*</sup> On sabbatical leave from Stanford University, Stanford, California 94305

# REACTIONS OF HO<sub>2</sub> RADICALS WITH HYDROCARBONS<sup>\*</sup>

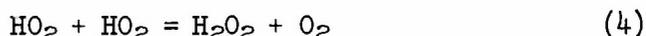
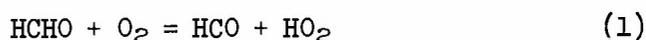
R. R. Baldwin and R. W. Walker

Department of Chemistry

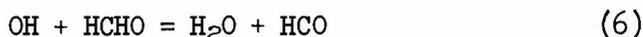
University of Hull

Hull, Yorkshire, ENGLAND

A simple mechanism for the oxidation of HCHO in aged boric-acid-coated vessels near 500°C may be suggested as



However, the oxidation is autocatalytic due to the homogeneous decomposition of the H<sub>2</sub>O<sub>2</sub> formed, the OH radicals continuing the chain through reaction (6).

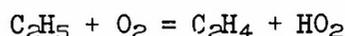


Although the ratio  $[\text{OH}] / [\text{HO}_2]$  will be low, OH radicals are very reactive and the system will not be a good source of HO<sub>2</sub> radicals for the study of reactions of the type,



In KCl-coated vessels, HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> are efficiently destroyed at the surface, so that reactions (5) and (6) will be unimportant, and the rate of oxidation of HCHO is found to be very reproducible.

The principle of the method may be simply illustrated for C<sub>2</sub>H<sub>6</sub>. It is well established that C<sub>2</sub>H<sub>5</sub> radicals are oxidized under the conditions used, by the reaction



so that

$$d[\text{C}_2\text{H}_4] / d[\text{CO}] = k_7 [\text{C}_2\text{H}_5] / k_2 [\text{HCHO}]$$

With C<sub>3</sub>H<sub>8</sub> and *i*-C<sub>4</sub>H<sub>10</sub>, alternative reactions of the alkyl radicals have to be taken into account.

Values of  $k_7/k_2$  have been obtained for C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and *i*-C<sub>4</sub>H<sub>10</sub> between 400° and 500°C. From the previously determined value of  $k_2$ , based on the ratio  $k_2/k_4^{1/2}$  and the known value for  $k_4$ , absolute determinations of  $k_7$  have been obtained. No other reliable estimates of  $k_7$  are available.

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<sup>\*</sup> Contract AF EOOAR 68-0013

## NONEQUILIBRIUM COMBUSTION PRODUCTS\*

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M.C. Branch, Research Assistant  
University of California  
Department of Mechanical Engineering  
Thermal Systems Division  
Berkeley, California 94720

This investigation has concerned itself with the identification of nonequilibrium combustion products, their kinetic behavior and their effect upon combustor performance. Current effort is focused upon the kinetics of reactions involving equilibrium and nonequilibrium product species. Recent results of kinetics in the N-H system have been reviewed and suggested rate data for reactions discussed.<sup>1</sup> The lack of data for ammonia decomposition particularly below 2000°K suggests further study. An experimental investigation of the homogeneous decomposition of ammonia in a high temperature flow reactor is in progress. A theoretical study of chemical nonequilibrium boundary layer flow in a circular duct<sup>2</sup> bears directly on the problem of interpreting kinetics in flow reactors.

The theoretical interpretation of kinetics is aided by a new procedure for integrating kinetic equations that has been developed which internally considers the possibility of steady state species.<sup>3</sup> The procedure results in a substantial reduction in computing time for a reaction mechanism including up to 30 elementary chemical reactions in addition to identifying the steady state species.

Future effort is planned for the experimental characterization of hydrocarbon system reactions at high temperature. Reaction kinetics and species concentrations in the oxidation of propane in a flow reactor will first be considered.

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\* Grant AF-AFOSR 1256-67

1. Branch, M.C. and Sawyer, R.F., "Review and Evaluation of Rate Data for Gas Phase Reactions of the N-H System," College of Engineering, University of California, Berkeley, Report No. TS-71-1, June, 1971.
2. Branch, M.C. and Sawyer, R.F., "Developing Duct Flow with Chemical Reaction," to be presented, 3rd International Colloquium on Gas Dynamics of Explosions and Reactive Systems, Marseille, France, September 12-17, 1971.
3. Laurendeau, N. and Sawyer, R.F., "General Reaction Rate Problems: Combined Integration and Steady State Analysis," College of Engineering, University of California, Berkeley, Report No. TS-68-4, June, 1968.

## IGNITION OF SIMPLE ALKANES IN SHOCK WAVES

Karl Scheller

Aerospace Research Laboratories

Wright-Patterson Air Force Base, Ohio 45433

Recent work in this laboratory on the ignition of methane, ethane and propane in oxygen-argon mixtures by shock waves is reviewed. Ignition delay times were measured and their concentration and temperature dependence determined in a single pulse shock tube using pressure, light emission and heat flux sensors behind the reflected shock wave.

The dependency of the ignition delay time on reactant concentration and mixture temperature was expressed in the customary manner as:

$$\tau = A \exp (E/RT) [\text{Ar}]^a [\text{F}]^b [\text{O}_2]^c$$

in which a, b and c are the power dependencies of the ignition delay times on the argon, fuel and oxygen concentrations respectively. This work differed from previous investigations in that the exponents were determined directly from experiment instead of by the usual trial and error fit.

To gain further knowledge of the chemistry of the ignition process, analyses were made of the gases behind the reflected shock for conditions in which the reaction was quenched shortly before and shortly after ignition. Product distributions as a function of temperature for all these fuels are presented and discussed.

The influence of additions of H<sub>2</sub> or C<sub>3</sub>H<sub>8</sub> upon the ignition of methane mixtures was investigated. Both were found to produce substantial reductions in the induction period, propane being about five times as effective as hydrogen on a molal basis. An explanation is advanced for this behavior.

Some comments are presented on a complete kinetic model for the oxidation of methane. Calculated and measured ignition delay times as a function of temperature and reactant concentration are compared.

SPECTROSCOPY OF SELECTED DIATOMIC METAL  
AND METAL-OXIDE MOLECULES\*

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Santa Barbara, California 93106

The techniques of laser excited fluorescence using both ~~cw~~ and pulsed lasers have been applied to the spectroscopic studies of MgO, PbO, BaO, AlO, Pb<sub>2</sub>, and Bi<sub>2</sub>. In addition, chemiluminescence has been observed for the following metal-oxides: BaO, AlO, MgO, SnO, BiO, and CaO.

Lifetimes of the A <sup>1</sup>Σ state of BaO have been measured for the vibrational levels v' = 0 to 11 from the fluorescence decay excited by a short-pulsed (10 nsec) tunable dye laser. Radiative lifetimes were found to vary with vibrational level from 0.275 ± 0.022 to 0.389 ± 0.016 μsec, with a value of 0.356 ± 0.007 μsec for v' = 0. Electronic transition moments and absorption oscillator strengths have been calculated from the measured lifetimes. Measured quenching cross sections of BaO(A <sup>1</sup>Σ) by helium vary with vibrational level by nearly an order of magnitude, from 0.28 to 2.28 x 10<sup>-16</sup> cm<sup>2</sup>, suggesting that part of the electronic quenching is through collisional transfer into a perturbing state. Consistent with this model of quenching is the fact that a second fluorescence decay, with a lifetime of 10 ± 2 μsec, is observed at high helium pressures from vibrational levels exhibiting strong quenching.

Intense fluorescence of AlO has been excited by two Ar<sup>+</sup> laser lines and is currently under investigation. Preliminary results of a lifetime study of AlO show the radiative lifetime to be about 130 nsec.

New molecular constants have been determined and spectral assignments made for Pb<sub>2</sub>. Fluorescence of the blue-green band system of Pb<sub>2</sub> was excited by an Ar<sup>+</sup> laser and the red system by a Kr<sup>+</sup> laser. To sufficiently simplify the Pb<sub>2</sub> spectrum for detailed analysis, it was necessary to use the Ar<sup>+</sup> laser in single mode operation.

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\* Project AF-AFOSR-70-1851

ENERGY TRANSFER PROCESSES IN GAS LASER MATERIALS\*

Daniel J. Seery

United Aircraft Research Laboratories

East Hartford, Connecticut 06108

The vibrational relaxation time has been measured for mixtures of HCl with the inert gases (He, Ne, Ar and Kr). The data were obtained by monitoring the  $3.5\mu$  emission from HCl following shock-heating of the gas mixtures. The exponential time constant for the growth of the emission signal gives the vibrational relaxation time.

The dependence of the vibrational relaxation time on the reduced mass of the collision pair is stronger than anticipated based on present theories. A normal reduced mass dependence for a V-T process is  $\ln \tau_p \propto \mu^{1/2}$  whereas the present data indicate  $\ln \tau_p \propto \mu^2$ . These measurements will be discussed in light of present theories of vibrational energy transfer and their significance in gas lasers will be outlined.

In addition some recent measurements of V-V transfer processes in HCl-CO and N<sub>2</sub>O-CO mixtures will be presented.

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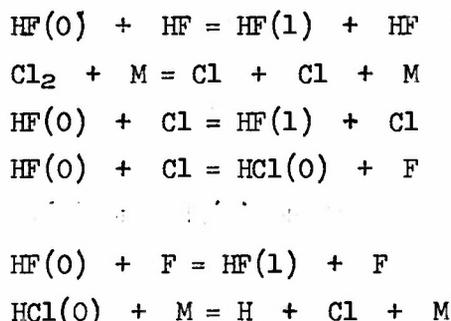
\* Project AF-OSR-F44620-69-0100

VIBRATIONAL EXCITATION OF DEUTERIUM FLUORIDE AND HYDROGEN  
FLUORIDE BY ATOMIC AND DIATOMIC SPECIES

W.C. Solomon

Air Force Rocket Propulsion Laboratory, Edwards, California

The vibrational excitations of HF<sup>1</sup> and DF and the energy transfer efficiencies for various collision partners were investigated over the temperature range of 1400°K to 4100°K. The extent of excitation was determined as a function of time by continuously monitoring the infra-red emission intensity at the center of the 1-0 vibration-rotation band of the molecule. Collisional efficiencies of HF, N<sub>2</sub>, O<sub>2</sub>, F, Cl, Br, H<sub>2</sub>O and DF in relaxing HF and of DF, HF, and N<sub>2</sub> in relaxing DF are reported.<sup>2</sup> A comparison of relaxation data for pure HF taken at elevated temperatures with data currently available from studies near room temperature suggests that long range attractive forces are mechanistically of major importance in the relaxation process. The very high efficiency of atomic chlorine in relaxing HF, i.e.  $(\tau P)_{\text{HF-HF}} / (\tau P)_{\text{HF-Cl}} = 70 \pm 15$  is discussed in terms of our previous result for atomic fluorine, i.e.,  $(\tau P)_{\text{HF-HF}} / (\tau P)_{\text{HF-F}} = 18$ . Relaxation profiles for the Cl-HF interaction have been conducted. The following mechanism is required to explain the data.



The  $(\tau P)_{\text{HF-HF}}^{1600^\circ\text{K}} / (\tau P)_{\text{HF-Br}} = 64$  and has a temperature dependence which is different from that operating in the HF-Cl interaction. The lack of a strong temperature dependence suggests that efficient E-V energy exchange mechanism may be operating during the interaction. The excitation of HF(v=1) is markedly catalyzed by the presence of H<sub>2</sub>O. Rapid equilibration through the rotational modes of water is presumed to be responsible for the latter behavior.

1. W.C. Solomon, J.A. Blauer, F.C. Jaye and J.G. Hnat, Int. J. Chem. Kin., 3, 215 (1971).
2. J.A. Blauer and W.C. Solomon, Int. J. Chem. Kin. (In press).

STUDIES OF EXCITED HYDROGEN IN RELATION  
TO ADVANCED PROPULSION<sup>\*</sup>

John M. Flournoy

Tetra Tech., Inc.

630 N. Rosemead Blvd., Pasadena, California 91107

The formation and disappearance of vibrationally excited hydrogen molecules are being investigated in fast-flowing streams of discharge-excited hydrogen. Excited  $H_2$  is monitored by observations of vibrational energy transfer to HCN, which then emits 3-micron infrared radiation (1).

In addition, an automated isothermal calorimeter has been built for catalytic thermal detection of the excited species. The platinum coil of the calorimeter also responds to H-atom combination, but preliminary results indicate that atoms and excited molecules can be distinguished by performing experiments at different flow rates.

Reproducibility of the measurements is still rather poor, apparently due to surface effects, and the two detection methods are not yet in quantitative agreement. However, the data do permit a calculation of the collision number for V-V transfer from  $H_2$  to HCN without knowledge of the absolute concentration of excited  $H_2$ .

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<sup>\*</sup> Contract AF-AFOSR-No. F44620-69-C-0080

1. J.M. Flournoy and L.Y. Nelson, Chem. Phys. Lett., 6, 521 (1970).

KINETIC CROSS SECTIONS FOR ELECTRON, ATOM  
AND MOLECULE COLLISIONS\*

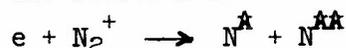
H. H. Michels

United Aircraft Research Laboratories

East Hartford, Conn. 06108

A computer code has been developed for predicting the elastic and inelastic cross-sections for electron-atom collisions in the energy range-zero to near threshold. This code is based on a non-arbitrary variational formulation for expansion-type scattering wavefunctions.<sup>1</sup> Part of this year's effort was in development of an efficient inelastic code and the documentation of the theoretical methods developed under this research. Results have been obtained for e-H and e-He scattering which indicate accuracies comparable to the best ever obtained, but with total computation times of only seconds. Future studies will involve application of these analytic methods to air species.

A study of the temperature dependence of dissociative-recombination kinetics in  $N_2$  is in progress. The reaction is



where  $N^*$  and  $N^{**}$  refer to possibly different excited states of the neutral N atom. Detailed calculations have been carried out for all possible dissociation channels. These studies indicate that only  $3\pi_u$  (and possibly  $3\Sigma_g^-$ ) symmetry states are involved in this reaction for thermal energy collisions. The products  $4S N + 2D N$  are indicated for sufficiently low-energy collisions. This reaction is coupled to NO and  $NO^+$  kinetics and future studies will involve energy transfer reactions between these species.

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\*Project AF-AFOSR-F44620-71-C-0066

1. F.E. Harris and H.H. Michels, Meth. in Comp. Phys. 10, 144 (1970).
2. C. Schwartz, Am. Phys. (N.Y.) 16, 36 (1961).

MOLECULAR ENERGY FROM A  
CROSSED BEAM EXPERIMENT\*

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Research Institute for Engineering Sciences

Wayne State University

Detroit, Michigan 48202

We are using a crossed molecular beam apparatus to measure molecular energies. The present emphasis is on electron affinities and bond energies. While the mechanism of the collision is of intrinsic interest (it requires the crossing of molecular potential-energy curves involving ionic and neutral electronic configurations), this talk will deal mainly with the energetics.

The experiment consists of accelerated cesium atoms striking the molecule of interest. The cesium atoms are normally in an energy range from 1-60 eV. This work may be compared with classic experiments involving collisions of electrons or photons with molecules, for which the Franck-Condon principle is closely obeyed. With the heavy (and slow) Cs, adiabatic transitions may take place. By measuring the threshold energy for a specific process we may determine the corresponding molecular energy.

In order to obtain the best possible energy resolution for the collision, we have developed a time-of-flight device. The energy of the Cs beam is determined from its flight time, and only those products which arrive within a desired range of time are counted. Those products formed from incorrect energies are rejected by means of appropriate gating. An automatic counting system is used to obtain the energy dependence of the cross section.

We have confirmed the well established electron affinity for  $O_2$ , and have resolved previously controversial values for the electron affinities of  $NO_2$ ,  $Br_2$ , and  $Cl_2$ .

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\* Grant AFOSR 69-1799

# COMBUSTION KINETICS OF REENTRY VEHICLE ABLATION MATERIALS<sup>\*</sup>

R. A. Matula

Thermal and Fluid Sciences  
Drexel University  
Philadelphia, Pennsylvania 19104

The thermal decomposition of carbonyl fluoride ( $\text{COF}_2$ ) in excess argon was studied behind shock waves in the temperature and total pressure ranges 2600-3600°K and 0.5 to 12 atmospheres respectively. The reaction was found and reported to be unimolecular in nature. Both Lindemann and RRK unimolecular reaction rate theories were used to analyze the observed rate constant variation with temperature and total pressure. The Lindemann unimolecular reaction rate theory was shown to best fit the experimental data and the experimentally observed rate constant was fit to the following equation which arises from the Lindemann theory

$$\frac{1}{K_{\text{obs}}} = \frac{1}{K_{\infty}} + \frac{1}{K_a [M]}$$

where

$K$  = high pressure limiting first order rate constant

$K_a$  = rate constant for collisional activation of the  $\text{COF}_2$  molecule.

The final reported values of  $K_{\infty}$  and  $K_a$  were represented as

$$K_{\infty} = (1.28 \pm 0.11) \times 10^{11} \exp\left(-\frac{93,270 \pm 14,510}{RT}\right)_{\text{sec}}$$
$$K_a = (1.15 \pm 0.08) \times 10^{12} \exp\left(-\frac{49,700 \pm 2,930}{RT}\right)_{\text{cc-mole}^{-1}\text{sec}^{-1}}$$

Preliminary shock tube studies of the thermal decomposition of  $\text{COF}_2$  in the presence of molecular hydrogen have been carried out in the temperature and pressure ranges 2700-3300°K and 1.9 to 3.0 atmospheres respectively. Preliminary results and mechanistic implications will be discussed.

The temperature dependence of the spectral and integrated intensity of the  $1943 \text{ cm}^{-1}$  infrared band of carbonyl fluoride was experimentally determined in the temperature ranges 300-600°K. The final value of the total integrated intensity,  $\alpha_{1943}$ , is independent of temperature and is reported to be

$$\alpha_{1943} = 4.11 \pm (0.07) \times 10^7 \text{ cm}^{-2} \text{-(moles/cc)}^{-1}$$

An expression for the temperature dependence of the theoretical band shape of the  $\nu_2$  fundamental vibration of  $\text{COF}_2$  was developed. Since the first overtone of  $\nu_1$  vibration is in Fermi resonance with the  $\nu_2$  vibration, the temperature dependence of the Fermi resonant contribution was evaluated. The Fermi resonance effects were combined with the theoretical band shape to predict the spectral intensity of the  $1943 \text{ cm}^{-1}$  band at temperatures above 600°K. In addition preliminary  $\text{C}_2\text{F}_4/\text{O}_2$  flame studies using a 2 inch flat flame burner will be discussed.

<sup>\*</sup> Grant AF-AFOSR-1606-68C

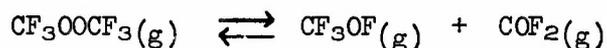
EQUILIBRIUM CONSTANTS FOR THE SYSTEM, BISTRIFLUOROMETHYL PEROXIDE,  
CARBONYL FLUORIDE, TRIFLUOROMETHYL HYPOFLUORITE\*

Joseph B. Levy and R. Craig Kennedy

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In 1957, Porter and Cady<sup>1</sup> reported that carbonyl fluoride,  $\text{COF}_2$ , and trifluoromethyl hypofluorite,  $\text{CF}_3\text{OF}$ , reacted between 250 and 300°C to give bistrifluoromethyl peroxide,  $\text{CF}_3\text{OOCF}_3$ . Their results indicated that the reactants and products were in equilibrium with each other in this temperature range.

In the present work this reaction has been examined from 220 to 350°C and equilibrium constants have been measured over this temperature range. The heat and entropy of reaction have been determined and, for the reaction



the values corrected to 298°C are:  $\Delta H^\circ = 24.6$  kcal.  $\Delta S^\circ = 37.5$  gibbs.

By combining these values with reported values for the reactants, the standard entropy and heat of formation of the peroxide have been found. This also gives access to the oxygen-oxygen bond strength in the peroxide which has been found to be about five kcal. mole<sup>-1</sup> greater than in alkyl peroxides. The results are discussed.

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\* AFOSR Grant 70-1939

1. R. S. Porter and G. H. Cady, J. Am. Chem. Soc., 79, 5628 (1957).

STUDIES OF REACTIONS OF FLUORINE  
CONTAINING COMPOUNDS

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Abstract not received in time to be included.

# CHEMICAL KINETICS OF FLUORINE COMBUSTION SYSTEMS<sup>\*</sup>

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## Vibrational Disequilibrium in Low Pressure Hydrogen-Fluorine Flames

Low pressure hydrogen fluorine flames diluted with 70% argon have been stabilized at 4 torr on a multidiffusion burner. The flame appears orange-red due to the emission from the upper vibrational levels of HF. A total of 21 vibration-rotation bands have been observed including the 6-0, 7-1, 8-2 and 9-3 transitions which have not been reported previously. The flame temperature calculated from the R and P branch of the 3-0 band are in good agreement. Temperature profiles of hydrogen rich, stoichiometric and fluorine rich flames have been determined. The maximum temperature of the stoichiometric flame is  $2700 \pm 150^\circ\text{K}$ , which is slightly less than the calculated flame temperature of  $2775^\circ\text{K}$ .

Of particular importance is the fact that the ratio of vibrational populations is roughly constant through the reaction zone. This is observed qualitatively from the ratio of intensity of the 4-0, 5-1, 6-2, 7-3, 8-4 and 9-5 series which is approximately the same in the beginning and end of the combustion zone. Quantitative measurements on the 3-0 and 4-1 bands show that the ratio of the fourth vibrational level to the third is decreasing slightly through the reaction zone. Under the specific conditions of the experiment there appears to be a steady state distribution of HF in the 3rd through 9th vibrational levels.

## Shock Tube Studies on the Rate of Dissociation of Tetrafluorohydrazine

The thermal dissociation of  $\text{N}_2\text{F}_4$  behind incident shock waves was studied at temperatures between  $390^\circ - 500^\circ\text{K}$ . Experiments were run with 1%  $\text{N}_2\text{F}_4$ -Ar gas mixture at pressures between 0.90-1.20 atm using Ar as the driver gas. The production of  $\text{NF}_2$  from  $\text{N}_2\text{F}_4$  was followed by monitoring the ultraviolet-absorption near  $2600^\circ\text{A}$  with a 0.25 meter monochromator. Results indicate a unimolecular mechanism, second order in the above pressure range. The rate constant is

$$k(\text{Ar}) = 10^{14.37} \exp -16.7 \text{ kcal mole}^{-1}/RT \text{ liter mole}^{-1} \text{ sec}^{-1}.$$

Preliminary experiments concerned with the effect of trace contaminants  $\text{O}_2$ ,  $\text{Cl}_2$  and  $\text{H}_2$  on the rate of the dissociation of  $\text{N}_2\text{F}_4$  were also conducted.

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<sup>\*</sup> Project AF-AFOSR 68-1523

DECOMPOSITION KINETICS OF THE ROCKET OXIDIZER AMMONIUM PERCHLORATE<sup>A</sup>

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The manner in which the pressure limit of ammonium perchlorate varies with additions of potassium permanganate as physical and co-crystallized mixtures has been measured. The time-honored go - no go experimental technique was used. The addition of potassium permanganate in the co-crystallized form had a much greater influence on the pressure limit.

Theoretical ignition transients were computed using a steady-state deflagration theory previously developed. Interesting characteristics which the theory exhibits are: minimum ignition flux strength for ignition, overshoot of temperature to a value higher than the steady deflagration temperature, "ignition" temperature depending upon strength of ignition flux.

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<sup>A</sup> Project AF-AFCSR-68-1458

THE USE OF OXYGEN-17 IN STUDYING  
THE PROPERTIES AND CHEMISTRY OF VARIOUS OXIDIZERS<sup>\*</sup>

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The electron paramagnetic resonance (EPR) spectra of  $\text{NO}_2$  were obtained in both the solid and liquid phases of the  $\text{NO}_2\text{-N}_2\text{O}_4$  system. The EPR signal changes markedly on freezing and evidence for super-cooling exists. In the liquid phase the equilibrium  $\text{N}_2\text{O}_4 = 2 \text{NO}_2$  is temperature dependent and the equilibrium may be studied by observing the EPR-active  $\text{NO}_2$ .

The EPR spectra of gas-phase  $\text{NO}^{16}$  and  $\text{NO}^{17}$  (mixed with  $\text{NO}^{18}$  and  $\text{NO}^{16}$ ) was observed at pressures of about 1 mm Hg. Significant differences in the EPR spectra are explicable in terms of changes in the mass of the oxygen isotope, giving rise to different orbital-spin coupling, and in terms of the nuclear hyperfine interaction with the  $\text{O}^{17}$  nucleus.

The oxygen-17 NMR spectra of  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_3$ , and  $\text{N}_2\text{O}_5$  are also being studied.

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<sup>\*</sup> Contract No. F44620-70-C-0027

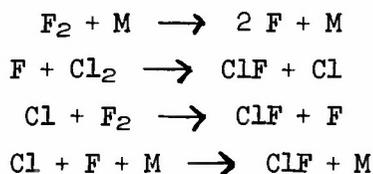
PHOTOCHEMISTRY OF INTERHALOGENS\*

A. E. Axworthy and K. H. Mueller

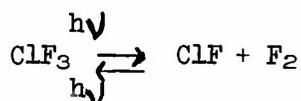
Advanced Programs North American-Rockwell  
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The photochemistry of fluorine, chlorine, and interhalogens such as  $\text{ClF}_3$  and  $\text{ClF}$  is under investigation. Experiments have been conducted using the entire spectral range from a mercury vapor lamp, and also selecting only the 365 nm band from the same lamp. In many of the experiments a gas chromatographic column, which was directly attached to the photochemical apparatus, was employed to follow the disappearance of reactants and the formation of products as a function of time. Good resolution was obtained for all constituents of interest except  $\text{F}_2$  and  $\text{N}_2$ .

Irradiation of  $\text{F}_2/\text{Cl}_2$  mixtures with 365 nm light at room temperature resulted in the formation of  $\text{ClF}$  and, with excess  $\text{F}_2$ , some  $\text{ClF}_3$ . However, the observed quantum yields were much less than one (based on  $\text{ClF}$  formed per quanta absorbed by  $\text{Cl}_2$ ). This result was unexpected because the low-temperature thermal reaction of  $\text{F}_2$  and  $\text{Cl}_2$  has been reported to proceed via the following long-chain reaction:



The photolysis of  $\text{ClF}_3$  to  $\text{ClF} + \text{F}_2$  at constant  $\text{ClF}_3$  concentration was initially rapid and then gradually slowed down, apparently approaching a photochemical steady-state:



in which the ratio  $\text{ClF}/\text{ClF}_3$  was about three. The addition of nitrogen slows the reaction very drastically and lowers the extent of reaction at the photochemical steady-state to a  $\text{ClF}/\text{ClF}_3$  ratio of only about one.

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\* Contract F44620-70-C-0094

RATES AND MECHANISMS OF  
REACTIONS OF FLUORINE CONTAINING  
ROCKET PROPELLANTS\*

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The study of the rate of pyrolysis of  $OF_2$  in a flow system was continued. Additional data were obtained showing that the lower than first-order rate of this reaction was not due to surface effects. Thus, lending support to the previous suggestion that the unimolecular decomposition of the OF radical contributes to the propagation of a chain mechanism coupled with a termination step of the recombination of OF radicals to produce  $O_2$  and  $F_2$ .

In the study of the rate of the  $OF_2$ - $H_2$  reaction, aluminum was used in place of monel for the reactor. It was found that the rates and surface effects were significantly reduced as compared to those obtained previously. The overall order of the fully inhibited reaction appears to be about 1.5, with the dependence on  $OF_2$  concentration somewhat larger than first-order and on  $H_2$  concentration close to zero-order. These investigations are continuing.

The study of the rate of the  $NF_2$ - $H_2$  reaction has been initiated.

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\* AFOSR Grant No. 1291-67

## INTERFACIAL CHEMICAL REACTIONS<sup>a</sup>

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This program is directed toward understanding the role of transport and kinetic phenomena in determining the rates of heterogeneous chemical and/or phase changes in energy conversion systems of aerospace importance. Recent theoretical studies are outlined in the following areas:

- A. Active-Passive Transition in Metal Oxidation
- B. Transient Vaporization and/or Combustion of Droplets in Dense Gases
- C. Kinetic Limitations to Bubble Growth in Supersaturated Solutions
- D. Inference of Gas/Metal Absorption Probabilities from Electrical Resistance Measurements
- E. Effect of Multiple Encounters on Inferred Gas/Solid Reaction Probabilities on Rough Surfaces

Using our microwave discharge/vacuum flow system/Langmuir filament techniques<sup>1,2</sup> we are currently studying the kinetics of nitrogen engassing and degassing of tantalum, with emphasis on the effects of gas phase dissociation on the absorption rate. Our recent experimental results and future plans will be described. Additionally, current experimental studies of (i) atom/liquid reaction kinetics and (ii) aerosol production downstream of oxidizing and/or subliming filaments, will be reviewed.

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<sup>a</sup> Project AF-AFOSR-F44620-70-C-0026

1. Rosner, D.E. and Allendorf, H.D., "Kinetics of the Attack of Refractory Materials by Dissociated Gases", Proc. International Conference in Heterogeneous Kinetics at Elevated Temperatures, Plenum Press, New York (1970) 231-251.
2. Rosner, D.E., "High Temperature Gas/Solid Reactions", Vol. 2, Annual Review of Materials Science (R.A. Huggins, ed.), Annual Reviews Inc., Palo Alto, Calif. (in preparation).

PROPERTIES OF ENERGETIC IONS TRAPPED IN SOLIDS:  
DRIFT MOBILITIES OF PHOTOEXCITED ELECTRONS IN GLASSY MATRICES\*

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Ionizing radiation produces ions which can often be trapped or stored in suitable solid matrices. The energy associated with these trapped ions can be released by optical or thermal excitation. In previous work, optical excitation of trapped electrons leading to photoconduction<sup>1</sup>, and optical bleaching<sup>2,3</sup> were examined. Photoconduction is observed but little is known about the transport and scattering mechanisms of mobile electrons in glassy matrices. Such information can be obtained from mobility studies. In 10 M NaOH glassy ice it turns out that "hot" electron effects are observed and that the mobile electrons behave very similarly to electrons in crystalline germanium or silicon. In organic glasses the mobilities are lower and hot electron effects are not observed.

Drift mobilities of photoexcited electrons have been measured with a xenon flash lamp and time-of-flight detection. Electric field and temperature have been varied. At low fields the drift mobility is independent of field. In the 10 M NaOH glassy ice at 77°K the drift mobility goes through a maximum near 0.5 kV/cm and then decreases as the reciprocal of the field at higher fields. This is precisely the behavior observed for electrons in germanium at 20°K and is characteristic of hot electron effects. The increase in the drift mobility with field is due to scattering from ionized species and the decrease at higher fields is due to lattice scattering, interaction with optical modes. The temperature dependence between 4°K and 130°K shows a mobility dependence on  $T^{-3/2}$  above 50°K which is characteristic of lattice scattering. At lower temperatures the mobility dependence is complex but fits well to what is expected for ionic species scattering.

The density of ionic species that is consistent with the observed mobility due to ionic scattering is about  $10^{18} \text{ cm}^{-3}$ . This is much smaller than the  $\text{Na}^+$  and  $\text{OH}^-$  concentrations in the glass so these ions seem to be incorporated into the conduction band structure and to not

contribute to the scattering of mobile electrons. However,  $O^-$  ions are also produced by gamma-irradiation of the glassy matrix. Their concentration is about  $10^{18} \text{ cm}^{-3}$  so the  $O^-$  "holes" appear to act as the ionic species scatterers.

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\* Project AF-AFOSR-70-1852

1. J. Eisele and L. Kevan, J. Chem. Phys., 53, 1867 (1970).
2. P. Hamlet and L. Kevan, J. Amer. Chem. Soc., 93, 1102 (1971).
3. H. Hase and L. Kevan, J. Chem. Phys., 54, 908 (1971).

ENERGY MIGRATION IN IRRADIATED SOLIDS

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Abstract not received in time to be included.

PRODUCTION AND MOLECULAR ENERGETICS OF HIGH ENERGY  
ROCKET PROPELLANT INGREDIENTS USING CRYOCHEMICAL ENGINEERING TECHNIQUES

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This program is devoted to an experimental and theoretical study of the efficacy of cryogenic temperature operations in the synthesis of purifyable compounds exhibiting energy and reactivity characteristics at the uppermost limits that can be imagined. It seems perhaps intuitively reasonable that such a reduction in the Boltzmann factor should improve the probability of isolating species which ordinarily appear as intermediates, if at all, in processes conducted at more ordinary temperatures.

A semi-empirical LCAO-MO-SCF scheme known as MINDO (modified intermediate neglect of differential overlap) developed elsewhere has been adapted to the N-O-F family, and it has successfully explained all of the known compounds and both the recent synthesis of  $O_2NNF_2$  in this laboratory and that of ONOF elsewhere. MINDO computations suggest the series of compounds,  $N(OF)_3$ ,  $NF(OF)_2$ , and  $NF_2(OF)$  should also be stable, but that other readily postulated compounds will all be unstable.

We have continued to study the elementary chemistry of aminoborane,  $H_2BNH_2$ , the isoelectronic analog of ethylene, following our recent successful synthesis, isolation, and characterization of the species. Several halogenated derivatives have been produced and characterized as has the unusual heterocycle,  $\overline{CH_2BH_2}NH_2$ . Because of the many comparisons with corresponding hydrocarbons, this family of compounds is of fundamental importance, and because of the obvious implications regarding a new family of inorganic polymers, this family may also have striking technological importance as well.