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10th AFOSR CONTRACTORS' MEETING ON KINETICS OF ENERGY CONVERSION

4 & 5 SEPTEMBER 1969

BERKELEY, CALIFORNIA

COLLEGE OF ENGINEERING
UNIVERSITY OF CALIFORNIA, Berkeley

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10th AFOSR CONTRACTORS' MEETING

ON

KINETICS OF ENERGY CONVERSION

4 & 5 September 1969

University of California at Berkeley

AGENDA

Thursday
4 September 1969

0900	REGISTRATION	277 Cory Hall
0920	WELCOME - HOST	R. Steidel, University of California, Berkeley
0930	WELCOME - AFOSR	J. Masi, AFOSR
0940	Calculations of Cross-Sections for Electron-Atom and Atom-Atom Collisions	H. H. Michels, United Aircraft Research Laboratories
1010	Intermolecular Potential Energies by Molecular Beam Scattering Method	E. W. Rothe, Wayne State University
1040	COFFEE BREAK	
1100	Elementary Reactions of Nitrogen - Hydrogen - Fluorine Systems	D. I. MacLean, Boston College
1130	Trapping and Detrapping of Radiation-Producted Electrons in Glassy Solids	L. Kevan, Wayne State University
1200	Combustion Kinetics of Tetrafluoroethylene	R. A. Matula, Drexel Institute of Technology
1230	LUNCH	
1345	Mass Spectrometric Investigation of the Synthesis, Stability, and Molecular Energetics of High Energy Molecules at Cryogenic Temperatures	H. A. McGee, Jr., Georgia Institute of Technology

Thursday
4 September 1969

1415	Advanced Oxidizer Chemistry	I. J. Solomon, IIT Research Institute
1445	Effects of Additives on Flame Propagation	R. L. Tischer, Aerospace Research Laboratories, WPAFB
1515	COFFEE BREAK	
1530	Kinetics of Reactions of Fluorine Containing Compounds	T. Houser, Western Michigan University
1600	Studies of Excited Hydrogen	J. M. Flournoy, Tetra Tech, Inc.
1630	The Kinetics of the Photochemical Reaction Between Fluorine and Carbon Dioxide	J. E. Sicre, National Research Council, Buenos Aires, Argentina
	The Kinetics of the Thermal Reaction Between CF_3OF and SO_3	J. E. Sicre, National Research Council, Buenos Aires, Argentina
1900	DINNER	

Friday
5 September 1969

0900	Studies of the Deuterium + Oxygen Reaction	R. R. Baldwin, University of Hull
0930	Vibrational Relaxation of CO_2 with Selected Collision Partners	D. J. Seery, United Aircraft Research Laboratories
1000	Optical Spectra Observed During Ion-Molecule Collisions with Low-Energy N_2^+ and Ar^+ Beams	H. P. Broida, University of California (Santa Barbara)
1030	COFFEE BREAK	
1045	Nonequilibrium Combustion Products	R. F. Sawyer, University of California (Berkeley)
1115	Physical Nature of Propellant Sensitivity	T. A. Erikson, IIT Research Institute
1145	Overall Reaction Rates of Paraffin Hydrocarbons	I. Glassman, Princeton University
1215	LUNCH	
1330	Theory of Heterogeneous Reactions in Flow Systems	D. E. Rosner, AeroChem Research Laboratories
1400	Kinetics of the Attack of Refractory Materials by Dissociated Gases	D. E. Rosner, AeroChem Research Laboratories
1430	Deflagration of Single Crystals of Ammonium Perchlorate	E. E. Petersen, University of California (Berkeley)
	ADJOURN	

10th AFOSR CONTRACTORS' MEETING

4 and 5 September 1969
University of California, Berkeley

ATTENDANCE LIST

T. Asmus	Western Michigan University, Kalamazoo, Michigan
R. R. Baldwin	Hull University, Hull, England
O. A. Berthold	HQ Air Force Systems Command, Andrews AFB, Maryland
Melvyn Branch	University of California, Berkeley
H. P. Broida	University of California, Santa Barbara
R. Brokaw	NASA Lewis Research Center
Frederick L. Dryer	Princeton University, Princeton, New Jersey
T. A. Erickson	IIT Research Institute, Chicago, Illinois
John M. Flourney	Tetra Tech, Inc., Pasadena, California
Eli Freedman	U.S. Army Ballistic Research Labs
Irvin Glassman	Princeton University, Princeton, New Jersey
R. W. Haffner	AFOSR
T. Houser	Western Michigan University, Kalamazoo, Michigan
L. Kevan	Wayne State University, Detroit, Michigan
Morton J. Klein	IIT Research Institute, Chicago, Illinois
Donald T. MacLean	Boston College, Chestnut Hill, Massachusetts
J. F. Masi	AFOSR, Arlington, Virginia
R. A. Matula	Drexel University, Philadelphia, Pennsylvania
Henry A. McGee, Jr.	Georgia Institute of Technology, Atlanta, Georgia
H. Michels	United Aircraft Research Laboratories, East Hartford, Conn.
Larry Muzio	University of California, Berkeley
E. E. Petersen	University of California, Berkeley

D. E. Rosner	AeroChem Research Labs, Princeton, New Jersey
E. W. Rothe	General Dynamics/Convair, San Diego, California
William H. Ruigh	AFOSR (SRC)
R. F. Sawyer	University of California, Berkeley
Daniel J. Seery	United Aircraft Research Labs, East Hartford, Conn.
J. Sicre	National Research Council, Buenos Aires, Argentina
I. Solomon	IIT Research Institute, Chicago, Illinois
W. Solomon	Air Force Rocket Propulsion Laboratory
D. R. Squire	U.S. Army Research Office, Durham, North Carolina
E. S. Starkman	University of California, Berkeley
R. L. Tischer	Aerospace Research Labs. WFAFB, Ohio

Calculation of Cross-Sections for Electron-Atom and Atom-Atom Collisions

H. H. Michels and H. J. Kolker

United Aircraft Research Laboratories, East Hartford, Conn. 06108

Collisional processes involving electrons, ions and neutral particles are being analyzed in the thermal scattering region using quantum mechanical techniques.[1] These studies are being undertaken to provide a better understanding of the reaction kinetics and transport properties of very hot gases.

The elastic scattering of slow electrons from hydrogen and helium has been studied using analytic procedures for representing the scattered electron.[2] Total elastic and momentum transfer cross-sections have been calculated and compared with experiment. In addition, an expansion approach has been formulated for the calculation of inelastic-scattering wavefunctions.[3] The method can be applied for any incident energy, including values at resonances resulting from stable or metastable bound states. Calculations have been performed for a model two-channel problem which illustrate the utility of the method.

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[1] Work sponsored in part under Contract AF 49 (638)-1711.

[2] H. H. Michels, F. E. Harris and R. M. Scolsky, Phys. Letters 28A, 467 (1969).

[3] F. E. Harris and H. H. Michels, Phys. Rev. Letters 22, 1036 (1969).

We have also initiated studies of the dynamics of resonant and non-resonant collisions between ions, atoms, and molecules. Certain of these studies are concerned with elastic scattering cross-sections and the rates of collisional excitation transfer.[4-6] The results have been compared with experimental molecular beam data in some cases.

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[4] H. J. Kolker and H. H. Michels, J. Chem. Phys. 50, 1762 (1969).

[5] H. H. Michels, F. E. Harris and J. C. Browne, J. Chem. Phys. 48, 2821 (1968).

[6] J. M. Peek, T. A. Green, J. Perel and H. H. Michels, Phys. Rev. Letters 20, 1419 (1968).

Intermolecular Potential Energies by a Molecular Beam Scattering Method*

Erhard W. Rothe

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Wayne State University
Detroit, Michigan 48202

Two types of work have been performed this year. The first has been an investigation of the electron-jump model of chemical reactions, the second is that described by the above contract title.

Physicists are alleged to think of chemistry as a neat demonstration of what may be done with electrons, nuclei, and Coulomb's law. We have studied a reaction which proceeds by a one-electron jump, i.e. the mechanism is $A+BC \rightarrow A^{+}+BC^{-} \rightarrow A^{+}B^{-}+C$. The term harpooning is widely used: A throws its electron, spears BC, and pulls it in with the Coulomb attraction, which results in a high-energy ionic collision. This mechanism has been suggested for a number of reactions, and previous experiments have been consistent with it. We have directly measured the intermediate A^{+}. This is impossible at thermal energies because, at large separation, the process is endothermic by an amount equal to the difference between the ionization potential of A and the electron affinity of BC, which is usually several eV. We have been able, to overcome this energy defect by supplying kinetic energy to A between 2 and 20 eV.

We have also continued our work at thermal energy on the measurements of intermolecular potential energies, and on further details of atom-molecule collisions. Approximately 90 systems have been studied.

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*Experimental work performed at General Dynamics/Convair under Contract AF49(638) - 1730.

Elementary Reactions of Nitrogen - Hydrogen - Fluorine Systems

Donald I. MacLean
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Chestnut Hill, Massachusetts 02167

Shock tubes and low pressure diffusion burners have been under development for the investigation of fluorine-containing systems. Ammonia/fluorine diffusion flames were studied briefly at atmospheric pressure to obtain data for the design of the relatively high capacity monitoring and pumping apparatus required for the low pressure flame. NH_4F is a main product of the ammonia-rich flame. A 1-meter grating vacuum ultraviolet spectrophometer was built and tested.

Vibrational-translational energy transfer in three dimensional atom diatom collisions has been studied using a "breathing" sphere model. The diatom was considered to be a Morse oscillator and the coupled Schrödinger equation solved numerically using an exponential representation. Some results of the calculations will be presented and discussed.

TRAPPING AND DETRAPPING OF RADIATION-PRODUCED ELECTRONS IN GLASSY SOLIDS*

Larry Kevan
Department of Chemistry
Wayne State University
Detroit, Michigan 48202

Electrons produced by photoionization or ionizing radiation can be trapped and stored in a number of inorganic and organic glassy solids. Detrapping can be initiated by optical or thermal excitation. In order to understand the trapping efficiency we have studied the spatial distribution of trapped electrons in matrices of different polarity and produced by different types of radiation. Paramagnetic relaxation has been used to measure relative spin - spin interactions which relate to the spatial distribution. For Co-60 γ-radiolysis in polar matrices such as ice and alcohols the electrons are trapped nonuniformly within regions about 40Å in radius; thus the trapped electrons reflect the initial nonuniform energy deposition by the γ-rays. In less polar matrices the electrons travel further before being trapped and approach a more uniform spatial distribution. Photoionization produces a uniform distribution of trapped electrons, even in polar matrices. Tritium β-radiation is more densely ionizing than Co-60 γ-rays. The β-radiation leads to lower yields of trapped electrons and a more uniform spatial distribution; this is consistent with some recombination occurring within the β-track. Current experiments deal with optical detrapping and the charge conduction process. Optical excitation of electrons in 10 M NaOH ice seems to occur directly to a conduction band. Photoconductivity is observed and the rate of optical bleaching shows a slight negative temperature dependence. An optical transition to an unbound state requires modification of previous theoretical treatments of trapped electrons in polar matrices. Future work will be directed toward photoconductivity studies and measurement of mobilities of photo-detrapped electrons.

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*Supported by Air Force Contract F04611-67C-0032 at the University of Kansas, Lawrence, Kansas.

COMBUSTION KINETICS OF TETRAFLUOROETHYLENE*

Richard A. Matula

Department of Mechanical Engineering
Drexel Institute of Technology
Philadelphia, Pennsylvania 19104

The design of an effective experimental program and the analysis of experimental data in high temperature combustion systems is often dependent on the availability of a wide variety of relatively complex computational capabilities. Therefore, during the past year, considerable effort has been expended in order to obtain these required capabilities. Representative computations from the following three classes of programs are discussed: (1) complex multi-element chemical equilibrium calculations; (2) calculation of the thermodynamic state behind either incident or reflected shock waves, based on either chemically frozen or equilibrium flow; (3) chemical kinetics calculations.

A three inch shock tube facility which has been designed for high temperature kinetic studies in the C/F/O system is described. The high temperature dissociation kinetics of CF_2O are presently being studied, and preliminary results are discussed.

The flame velocities of mixtures of tetrafluoroethylene (C_2F_4), perfluoropropene (C_3F_6), perfluorocyclobutene ($c\text{-}C_4F_6$) and perfluorocyclobutane ($c\text{-}C_4F_8$) with oxygen at atmospheric pressure are reported. The peak flame velocity of fluorocarbon-oxygen mixtures cannot be correlated with the peak calculated adiabatic flame temperature, but it is shown that the peak burning velocity can be correlated with maximum equilibrium fluorine atom concentration. These results indicate that the flame propagation mechanism in fluorocarbon-oxygen systems is dominated by diffusion of reactive fluorine atoms from the hot products into the unburned reactants rather than by thermal effects.

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*Grant AF-AFOSR-68-1606

Mass Spectrometric Investigation of the Synthesis, Stability, and Molecular Energetics of High Energy Molecules at Cryogenic Temperatures*

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Georgia Institute of Technology
Atlanta, Georgia 30332

This program is concerned with the study of novel combinations of plasma excitation and cryogenic quench techniques for the synthesis of small molecules, generally of the first row elements, which exhibit unusual reactivity or energetic behavior. Most of these product species will exist as stable reagents only below some rather low critical temperature.

A variety of these techniques have been employed in a search for compounds of the lighter noble gases, but a successful synthesis and energetic characterization was found for only KrF_2 (P. A. Sessa and H. A. McGee, Jr., J. Phys. Chem. 73, 2078 (1969)). BH_3 was found to be readily produced in good yield from BH_3CO, and the energetic characterization of this interesting hydride was accomplished (P. S. Ganguli and H. A. McGee, Jr., J. Chem. Phys. 50, 4658 (1969)). Studies of the synthesis and energetics of HBNH and H_2BNH_2 have continued, as have studies of the chlorinated and fluorinated derivatives of these species. These are, of course, the BN isoelectronic analogs of acetylenes and ethylenes. The use of O_2F_2 as a reagent at cryogenic temperatures for introducing the O_2F moiety into a series of substrate molecules has been disappointing. Exploratory studies of the possible existence of heretofore unknown phases or modifications of certain elements and compounds to be produced by cryoquench techniques has also been disappointing. New instrumentation and apparatus has been developed which permits convenient mass spectrometric analysis and ionization efficiency measurements at cryogenic temperatures with no associated warm-up (J. K. Holzhauer and H. A. McGee, Jr., Anal. Chem., in press, scheduled September 1969).

The highlights of all of these activities will be reviewed.

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*Research supported by grant AF-AFOSR-1308-67.

ADVANCED OXIDIZER CHEMISTRY

by
I.J. Solomon, A.J. Kacmarek, and J.N. Keith

IIT Research Institute
Chicago Illinois 60616

It has been postulated that the reaction of COF_2 and OF_2 to yield CF_3OOOCF_3 proceeds by the following mechanism:

$$COF_2 + MF \longrightarrow M^+ \; OCF_3^-$$

$$OF_2 + CF_3O^- \longrightarrow CF_3OOF + F^-$$

$$CF_3OOF + CF_3O^- \longrightarrow CF_3OOOCF_3 + F^-$$

The mechanism of the reaction was determined by means of O-17 tracer techniques as well as conventional means.

The following reactions will also be discussed:

$$CF_3CF{=}CF_2 + O_2F_2 \longrightarrow CF_3CF_2CF_2OOF + CF_3CF(OOF)CF_3$$

$$O_2F_2 + ClF \longrightarrow O_2ClF_3 \; ?$$

$$O_4F_2 + SO_2 \longrightarrow FSO_2OOF + \ldots.$$

AFOSR Contract No. F44620-68-C-0039

EFFECTS OF ADDITIVES ON FLAME PROPAGATION

R. L. Tischer and K. Scheller

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W-PAFB, Ohio 45433

Experimental studies are reported of the effect of additives on the combustion characteristics of hydrocarbon-oxygen-nitrogen and hydrogen-chlorine mixtures. These investigations are of interest not only for the insight they might afford into the mechanisms and kinetics of flame reactions but for the potential technological benefit they might yield if they resulted in the development of techniques for accelerating or retarding combustion processes as desired for particular applications.

It has been suggested that burning velocity inhibitors in hydrocarbon flames exert their effect by reducing the hydrogen atom concentration. To examine this concept, an investigation was undertaken of the effect of various known inhibitory compounds on the flame speed of hydrogen-chlorine mixtures. It was hoped that the simpler kinetics of this system would permit a more ready explanation of their behavior than is possible for hydrocarbons. Some sixteen additives were tested in all, including the Group IVa and Va halides and the chlorinated methane series. Contrary to expectations, most of them increased the burning velocity. Possible explanations for their behavior are discussed.

In a parallel work, the hypothesis that halogens inhibit hydrocarbon flames by increasing the ignition temperature was subjected to experiment. A systematic determination was made of the effect of twenty halogen-containing additives on the hot wire ignition temperature of propane and methane-oxygen-nitrogen mixtures. The experimental data was rather surprising. Some of the compounds increased, a few decreased and many did not affect the ignition temperature. The kinetic implications of these findings are discussed in preliminary fashion. Plans for future ignition studies are outlined briefly.

Kinetics of Reactions of Fluorine Containing Compounds*

Thomas Houser and Thomas Asmus

Chemistry Department, Western Michigan University, Kalamazoo, Mich. 49001

The flow system for the study of the pyrolysis of OF_2 and the OF_2-H_2 reaction has been put into operation.

The rate data for the pyrolysis of OF_2 can be fit, approximately, by a pseudo 1st-order rate expression, the constant for which can be represented by the following equation:

$$k = 10^{11.2} \exp(-35,400/RT) \text{ sec}^{-1}$$

The addition of F_2 and O_2, the products of OF_2 pyrolysis, has shown that F_2 inhibits the pyrolysis rate significantly, whereas O_2 has no measurable effect on the rate. An increase in the reactor surface area to volume ratio by a factor of 2 also had no significant effect on the rate of reaction.

Since the overall rate appears approximately pseudo 1st-order (i.e. below the high pressure limit for a unimolecular process) although the reaction rate is retarded by product, the reaction mechanism must be complex. A detailed examination of the rate vs concentration of OF_2 data confirms this. It has not been possible for these investigators to devise a non-chain mechanism to account for inhibition without the introduction of a step which appears to have a low probability of occurrance. In addition, rate data obtained at subatmospheric pressures indicates a lowering of rate with total pressure (fixed reactant concentration) which is not linear. This may be due to the reaction being in the intermediate region between 1st- and 2nd-order, or due to the rate being dependent on steps, some of which are not influenced by total pressure.

Considering all of the kinetic and thermochemical information the following mechanism appears to be the most reasonable at this time.

Initiation $OF_2 + M \longrightarrow OF + F + M$ (1)

Propagation $OF_2 + F \rightleftarrows F_2 + OF$ Inhibition (2)

Propagation $2OF \longrightarrow O_2 + 2F$ (3)

Termination $2OF + M \longrightarrow O_2 + F_2 + M$ (4)

Termination $2F + M \longrightarrow F_2 + M$ (5)

The rate is given by the following equation, after steady-state treatment of the radicals and a suitable approximation:

$$\text{rate} = k_1 OF_2 M - k_{-2} F_2 (k_1 OF_2/k_4)^{1/2} - k_2 OF_2^2/4k_5 Mb + \frac{k_2 OF_2}{4k_5 Mb} \left\{ k_2^2 OF_2^2 + 8k_5 Mb \Big[k_1 OF_2 M + k_{-2} F_2 \left(\frac{k_1 OF_2}{k_4}\right)^{1/2} + \frac{2k_1 k_3 OF_2}{k_4} \right\}^{1/2}$$

where $b = (k_3/k_4 M) + 1$

This mechanism is not totally satisfactory and work is continuing.

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* Grant AF-AFOSR-1291-67

Abstract Prepared for 10th AFOSR Contractors' Meeting on Kinetics of Energy Conversion, Berkeley, Sept. 4-5, 1969.

STUDIES OF EXCITED HYDROGEN*

John M. Flournoy

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A stream of hydrogen, after passage through an electric discharge, ordinarily contains a very high concentration of atomic hydrogen but apparently very few vibrationally excited molecules. This is in direct contrast with discharged notrogen, in which the exit stream may typically contain about 5% atoms and 50% vibrationally excited molecules. The difference between the behavior of H_2 and N_2 is due to a fundamental difference in the mechanism of dissociation of the two species in the plasma. The lifetime of $H_2(v = 1)$ is long enough to permit its detection in our apparatus if it were present in significant quantities, once the atoms have been removed from the stream. We are using catalytic thermal probes, and titration with NO (with observation of the resultant red emission) to monitor the H-atom concentrations. We also plan to use Wrede gauges in this connection.

Detection of $H_2(v = 1)$ by calorimetric probes and NO titration to remove atoms (in analogy with the work of Morgan and Schiff with N_2) is complicated by the possibility that the platinum probe may also respond to the reaction of H with HNO or possible to HNO itself. The results of this type of experiment have, so far, been ambiguous and difficult to interpret.

The best evidence for the presence of some $H_2(v = 1)$ has been obtained by mixing HCN with the excited hydrogen stream and observing the HCN vibrational transition (001 → 000) by detection of the emission at 3.02 microns. The 001 state is selectively pumped by collisional energy transfer from H_2 (v = 1), possibly going through the 011 combination level, which is resonant with the excited H_2, or by direct excitation of the 001 state. The excited H_2 appears to be formed through atom recombination on uncoated Pyrex walls. Titration of the atoms with NO quenches the 3.02-micron radiation, and the signal is much weaker if the walls are coated with a fluorocarbon. The effects of other coatings are being studied.

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*Contract No. F44620-69-C-0080

"The kinetics of the photochemical reaction between fluorine and carbon dioxide".-

A.H.Jubert, J.E.Sicre and H.J.Schumacher.

Instituto de Investigaciones, Facultad de Ciencias Exactas,
47 y 115, Universidad Nacional La Plata, Argentina.

The photochemical reaction between F_2 and CO_2 was studied in the temperature range from 80 to 135°C. It is a homogeneous gas phase reaction yielding CF_3OF and O_2 as reaction products. The quantum yield is in general lower than 0.1 molecule/$h\nu$. The reaction rate is first order with respect to CO_2 pressure and depends on the square root of light intensity. The reaction rate increases with the total effective pressure. Oxygen inhibits the reaction strongly. Results are interpreted with the following reaction scheme:

(1) $F_2 + h\nu \rightarrow 2F$; (2) $F + CO_2 + M = FCO_2 + M$;

(2a) $FCO_2 \xrightarrow[k]{F} CF_3OF + \frac{1}{2} O_2$; (3) $F + F + M' = F_2 + M'$;

(4) $F + O_2 \rightarrow FO_2$; (5) $FO_2 + F = F_2 + O_2$.

On assuming that fluorine atom consumption by reactions (2) and (2a) is negligible as compared to reactions (3) and (5) the following rate equation is derived from the postulated mechanism:

$$+\frac{d[CF_3OF]}{dt} = \frac{P_{ef}.[CO_2].I_{abs}^{1/2}}{\sqrt{\frac{P_{ef}}{k'^2} + \frac{[O_2]}{k''^2}}}$$

where: $k' = k_2/k_3$; $'' = k_2/(k_5^{\frac{1}{2}} K^{\frac{1}{2}})$ and $K = k_4/k'_4$.

If $q_3 \approx 0$, from the temperature coefficient of k' the activation energy of reaction (2) results: $q_2 = 10.9 \pm 0.3$ kcal/mole.

GRANT: AF-AFOSR 1446-68

"The kinetics of the thermal reaction between CF_3OF and SO_3"

J.Czarnowski, E.Castellano and H.J.Schumacher

Instituto Superior de Investigaciones, Facultad de Ciencias Exactas, 47 y 115, Universidad Nacional La Plata, Argentina.

The thermal reaction between CF_3OF and SO_3 was studied between 203 and 234°C. It is a homogeneous gas phase reaction yielding as main reaction products CF_3OOSO_2F, $(CF_3O)_2$ and $F_2S_2O_6$. Traces of COF_2, SO_2F_2 and O_2 are also formed due to the thermal decomposition of the main products. The relative amount of these substances increases with reaction temperature.

At temperature lower than 235°C, in the presence of 20-40 torr of $F_2S_2O_6$, CF_3OOSO_2F is practically the only reaction product. Under these conditions the following rate equation is obtained:

$$-\frac{d[CF_3OF]}{dt} = -\frac{d[SO_3]}{dt} = +\frac{d[CF_3OOSO_2F]}{dt} = -\frac{dp}{dt} = k[CF_3OF]$$

The total pressure as well as the pressure of added inert gases have an specific effect on the reaction increasing slightly the reaction rate. Oxygen gas has no chemical effect.

Results can be interpreted with the following reaction scheme:

(1) $CF_3OF \rightarrow CF_3O + F$; (2) $F + SO_3 \rightarrow FSO_3$

$2\ FSO_3 \rightleftharpoons F_2S_2O_6$; (3) $CF_3O + FSO_3 = CF_3OOSO_2F$

(4) $CF_3O + CF_3O = CF_3OOCF_3$

On assuming $[FSO_3] \gg [CF_3O]$, the following rate equation is derived from the postulated mechanism:

$$-\frac{d[CF_3OF]}{dt} = +\frac{d[CF_3OOSO_2F]}{dt} = -\frac{dp}{dt} = k_1[CF_3OF]$$

By extrapolating k_1 to infinite pressure, at three different temperatures, the following rate equation results:

$$k_{1\infty} = 2.50 \times 10^{14} \exp\left(\frac{-43500 \pm 500}{RT}\right) \text{ sec}^{-1}$$

GRANT: AF-AFOSR 1446-68.-

STUDIES OF THE DEUTERIUM + OXYGEN REACTION*

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ENGLAND

Study of the $D_2 + O_2$ system is of interest, first because it provides information on isotope effects in the reactions involved in the $H_2 + O_2$ reaction, secondly because it provides a source of D and OD radicals with which to investigate isotope effects in the reactions of these radicals with additives, and thirdly because it can be used to investigate the mechanism of the elementary steps involved in hydrocarbon oxidation.

Previous studies of the $H_2 + O_2$ reaction in aged boric-acid-coated vessels have shown that to define the behaviour of the system in the temperature range 460 - 540°C, seven parameters, k_7, k_2/k_4, k_{14}/k_2, k_{15}/k_1, $k_{11}/k_{10}^{\frac{1}{2}}$, $k_8/k_2k_{10}^{\frac{1}{2}}$ and k_{14}/k_{14a}, are required. In the case of the $H_2 + O_2$ system, two of these can be obtained by independent studies of the decomposition of H_2O_2, and of the sensitising effect of H_2 on this decomposition. In the case of the $D_2 + O_2$ system, this method is not possible as pure D_2O_2 is not available, and alternative methods of obtaining these parameters have been devised.

The value of k_2/k_4 is obtained from a study of the second limit of $D_2 + O_2$ mixtures in KCl-coated vessels. The remaining four parameters have been evaluated from a study of the $D_2 + O_2$ reaction in aged boric-acid-coated vessels. Computer calculations have shown that the second limit is determined predominantly by the parameters k_7, k_2/k_4, and $k_8/k_2k_{10}^{\frac{1}{2}}$, so that $k_8/k_2k_{10}^{\frac{1}{2}}$ can be obtained from such studies. The induction periods are determined mainly by the parameters k_7, k_2/k_4 and $k_{11}/k_{10}^{\frac{1}{2}}$, so that $k_{11}/k_{10}^{\frac{1}{2}}$ can be obtained from such measurements. The maximum rate of the

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* Contract AF EOAR 68-0013

slow reaction is effectively determined by k_7, k_2/k_4, $k_{11}/k_{10}^{\frac{1}{2}}$, k_{14}/k_2 and k_{15}/k_1, so that the two remaining unknowns k_{14}/k_2 and k_{15}/k_1 can be determined in this way.

$OH + H_2 = H_2O + H$ (1)
$H + O_2 = OH + O$ (2)
$O + H_2 = OH + H$ (3)
$H + O_2 + M = HO_2 + M$ (4)
$H_2O_2 + M' = 2OH + M'$ (7)
$H + HO_2 = 2OH$ (8)
$2HO_2 = H_2O_2 + O_2$ (10)
$HO_2 + H_2 = H_2O_2 + H$ (11)
$H + H_2O_2 = H_2O + OH$ (14)
$H + H_2O_2 = H_2 + HO_2$ (14a)
$OH + H_2O_2 = H_2O + HO_2$ (15)

Vibrational Relaxation of CO_2 with Selected Collision Partners*

Daniel J. Seery
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East Hartford, Connecticut 06108

Recent studies of molecular energy transfer rates have indicated that for some collision pairs long-range attractive forces can have a large effect on near-resonant vibration-vibration energy transfer.

Mahan has suggested that near-resonant vibration-vibration energy transfer between strongly infrared-active vibrational levels should be much more probable than between inactive or weakly active vibrations because of the long-range dipole-dipole interaction. Moore has recently verified this prediction experimentally.

A series of experiments has been undertaken to provide information on vibration-vibration energy transfer rates for CO_2-CO and CO_2-HCl. These collision pairs were selected for their potential interest in gas laser systems and also to provide a test for energy transfer theories that include long-range forces.

The experimental technique consists of time-resolved measurements of infrared emission following shock-heating of the gas mixture. The apparatus consists of a 5.6" diameter shock tube specifically designed for operation at low post-shock pressures with low impurity levels. Infrared emission from a specific energy level is measured by fast-response Ge-Au and Ge-Cu detectors. This emission intensity is a direct measure of the population of the energy level. The exponential time constant of the emission signal is then related to the vibrational relaxation time.

In the studies on CO_2-CO vibrational energy transfer it is necessary to know the rates of reactions (1), (2) and (3) in order to estimate the rate of (4).

$$CO_2(000) + CO_2(000) \rightarrow CO_2(010) + CO_2(000) \quad (1)$$

$$CO_2(010) + CO_2(000) \rightarrow CO_2(001) + CO_2(000) \quad (2)$$

$$CO(v=0) + CO(v=0) \rightarrow CO(v=1) + CO(v=0) \quad (3)$$

$$CO_2(001) + CO(v=0) \rightarrow CO_2(000) + CO(v=1) \quad (4)$$

Reliable experimental data are available for (1), (2) and (3) and additional measurements are being made in the present study.

The experimental procedure will be discussed and some initial results on the CO_2-CO system will be presented.

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*Contract F44620-69-C-0100

Optical Spectra Observed During Ion-Molecule Collisions with Low-Energy N_2^+ and Ar^+ Beams*

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A spectroscopic study has been made of the light emitted during ion-molecule collisions using Ar^+ and N_2^+ beams at laboratory energies ranging from 10 to 1000 eV. Target gases for both ions included H_2, D_2, CO, N_2, O_2, NO, N_2O, CO_2, CH_4, and C_2H_2; in addition, He, Ne, Ar, and Kr were used as N_2^+ targets. Preliminary spectra of the reactions $He^+ + CO_2$ and $Ar^+ + Ar$ were also obtained. Photon emission in the visible and near ultraviolet was found to be a common occurance for ion-molecule reactions in this energy range.

Several different types of reactions have been found which lead to electronically, rotationally, and vibrationally excited states. Absolute cross sections for the production of some of the bright features observed in these reactions have been measured. They lie in the range of 10^{-17} cm^2 to 10^{-16} cm^2 at beam energies of several hundred eV, and decrease with decreasing beam energy. For some of the reactions, structure has been observed in the cross section versus energy curves.

Rotational and vibrational excitation of the collision products have been studied. In general, the rotational excitation increased as the energy of the bombarding ion decreased. No general trends were found in the vibrational excitation or in its energy dependence.

*Contract AF 04(611)11538

NONEQUILIBRIUM COMBUSTION PRODUCTS*

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Nonequilibrium components have been identified in the combustion products of rocket propellants.[1] This work is part of a continuing study of the identity, significance, prediction techniques, and reaction kinetics of nonequilibrium products.

Rocket propellant performance calculations generally are based on an assumption of an equilibrium initial condition for the nozzle expansion process. The significance of departures from this assumption were tested through calculation of propellant performance based on selected nonequilibrium initial conditions coupled with frozen, equilibrium, and kinetic nozzle flows.[2] Effects comparable to those attributed to boundary layers, nonuniform propellant mixtures, and kinetic nozzle expansion processes were noted.

Experimental studies of global reaction kinetics utilizing a flow reactor have been initiated. A point sampling technique and mass spectrometric gas analysis are employed. Initial studies are of the decomposition of ammonia in the 1200°K temperature region.

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* Grant AF-AFOSR 1256-67

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[2] Branch, M. C. and Sawyer, R. F., "Nonequilibrium combustion effects on propellant performance with equilibrium, kinetic, and frozen nozzle flow," AIAA Paper No. 69-469, AIAA 5th Propulsion Joint Specialist Conference, U.S. Air Force Academy, Colorado, June 9-13, 1969.

PHYSICAL NATURE OF PROPELLANT SENSITIVITY

by
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This program has had for an objective the detailed study and evaluation of vapor-supply by means of the forced vaporization process. The physical nature of liquid propellant sensitivity problems is better understood by an appreciation of the factors that influence vaporization, vapor-supply and change-in-state processes.

Quantitative data on the rate of forced vaporization for four inert liquids (water, carbon tetrachloride, butanol and chlorobenzene) are reported for several steady pressure levels (less than equilibrium), three bath temperatures (50, 25 and about 4°C) and five circular tube geometries (from 1.9 to 9.5 mm radius). Computer analysis was performed to correlate variables within the principles proposed by a new approach to steady state thermodynamics.* For each liquid temperature, a correlation coefficient of better than 0.99 was found for the following variables --- Z, steady mass flow per unit tube area; X, logarithm of the equilibrium to steady pressure ratio; and Y, reciprocal tube radius --- in an equation of the form,

$$Z = A X + B X Y \qquad (1)$$

The significance of the coefficients are discussed with respect to their variations with respect to liquid and temperature. Some ideas evolve which can be used as a basis for a fundamentally different approach to understanding vapor-supply mechanisms as applied to liquid propellant sensitivity problems.

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*Ralph J. Tykodi, THERMODYNAMICS OF STEADY STATES, Macmillian Co., New York, (1968).

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Overall Reaction Rates of Paraffin Hydrocarbons[*]

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The turbulent flow reactor employed in previous overall rate investigations was adapted to study the oxidation reactions of paraffin hydrocarbons.

The principal effort to date has been concerned with the determination of an overall rate expression for the oxidation of methane. The reaction has been studied at one atmosphere total pressure in the temperature range of $1200^{o}K - 1400^{o}K$. Results were obtained with oxygen rich mixtures diluted by large concentrations of nitrogen. Expressing the results in terms of a simple Arrhenius expression gives the following overall specific rate constant:

$$k = 10^{15.3 \pm 0.2} \exp \left\{ \frac{-62.5 \pm 1.00 \text{ KCAL/MOLE}}{RT} \right\} \left(\frac{\text{MOLE}}{\text{CM}^3} \right)^{-.5} \left(\text{SEC} \right)^{-1}$$

The order of the reaction was found to be 0.7 with respect to methane and 0.8 with respect to oxygen. These results will be discussed and compared in detail with those of other investigators.

Experiments with propane are presently underway, and the study of this reaction will constitute the next major effort.

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THEORY OF HETEROGENEOUS REACTIONS IN FLOW SYSTEMS*

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Consequences of the interplay between finite rate heterogeneous transformations and molecular diffusion are under theoretical investigation. Recent developments in the following areas of propulsion and/or aerospace interest will be outlined:

1. Zirconium Droplet Combustion[1]
2. Heat and Mass Transfer from Spheres
   a. Condensation-enhanced vaporization[2]
   b. Solidification of radiation-cooled droplets
   c. Dissolution of particles[3] and bubbles
3. Nucleation in Mixing Layers
   a. Fog or trail forecasting[4]
   b. Condensation trail lengths

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* Contract AF 49(638) 1654

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[1] Nelson, L. S., Rosner, D. E., Kurzius, S. C. and Levine, H. S., Twelfth Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, 1969), pp. 59-70.

[2] Epstein, M. and Rosner, D. E., Int. J. Heat Mass Transfer (in press); also, Trans. Met. Soc. AIME 242, 2355 (1968).

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KINETICS OF THE ATTACK OF REFRACTORY MATERIALS BY DISSOCIATED GASES*

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Microwave discharge/fast vacuum flow system techniques are being exploited to generate well defined streams of reactive atoms and free radicals for studies of gas/solid reaction kinetics.[1] By these means heterogeneous reactions can be investigated at filament temperatures up to the sublimation threshold of refractory materials under conditions such that the observed rates are no longer limited by (i) dissociative adsorption of diatomic gases on partially covered surfaces or (ii) reactant access or product escape by diffusion. Following a brief review of the techniques employed to generate and detect atoms/free radicals of interest,[2] we outline recent results on the attack of silicon carbide[3] by O-atoms, N-atoms (and mixtures[4] thereof) and the comparative attack of graphite[5] by O, O_2, OH, and H. Kinetic and aerospace implications of these results will be discussed.

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1. Rosner, D. E. and Allendorf, H. D. a) J. Electrochem. Soc. 114, 305 (1967) b) J. Phys. Chem. 69, 4290 (1965) c) Proc. Third International Symposium on High Temperature Technology, Butterworths (London) (in press) d) AIAA J. 6, 650 (1968) e) J. Chem. Phys. 49, 5553 (1968).

2. Rosner, D. E. and Allendorf, H. D., Paper to be presented at the International Conference on Heterogeneous Kinetics at Elevated Temperatures, University of Pennsylvania, September 8-10, 1969.

3. Rosner, D. E. and Allendorf, H. D., J. Phys. Chem. (submitted).

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5. Allendorf, H. D. and Rosner, D. E., Carbon (in press).

DEFLAGRATION OF SINGLE CRYSTALS OF AMMONIUM PERCHLORATE

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ABSTRACT

The purpose of this research project is to study the deflagration, ignition and quenching properties of large pure and doped single crystals of ammonium perchlorate in order to understand better the sequence of chemical steps which occur during the deflagration process.

Comparison of burning rates of large single crystals prepared in this laboratory with those prepared in another laboratory indicated the possibility that catalytically active impurities were present in the single crystals grown from AP from different sources even though the impurity concentration was extremely low.

Accordingly, a study was made to find the effect, if any, of impurities on the deflagration rate of ammonium perchlorate. Burning rates of polycrystalline pellets of ammonium perchlorate from three sources and with different degrees of recrystallization were measured and compared. The burning rate changed considerably in the first three successive recrystallizations and the data showed that the impurities affected the burning rate especially at high pressures. It was also found that occluded water in ammonium perchlorate pellets changed the deflagration rate considerably. These results indicate that one of the reasons for the disagreement among different investigators on the burning rate of ammonium perchlorate might well be the effect of traces of residual impurities which existed in the crystals and pellets used in the studies even after purification by recrystallization.

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13. ABSTRACT

This report consists of the agenda and abstracts of 21 papers presented at the Tenth Annual Contractors' Meeting on Kinetics of Energy Conversion held at the University of California, Berkeley on 4-5 September 1969. The abstracts describe work now in progress under the sponsorship of the Propulsion Division, Directorate of Engineering Sciences, AFOSR. Subjects discussed in the papers included the following: hydrogen-oxygen reactions, fluorine reactions, reactions in flames, atomic and molecular beam studies, combustion kinetics, matrix isolation studies, propellant sensitivity, vibrational and electronic relaxation, and lifetimes of metastable species.

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