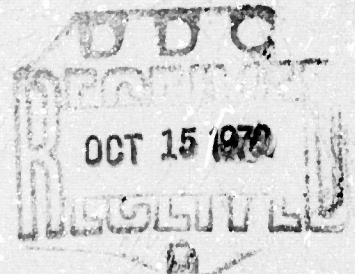


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ABSTRACTS OF PAPERS



11th AFOSR Contractors' Meeting
on
Kinetics of Energy Conversion

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AFOSR-70-2232-TR

3-4 September, 1970



GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

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11th AFOSR Contractors' Meeting
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11TH AFOSR CONTRACTORS' MEETING
on
KINETICS OF ENERGY CONVERSION

3-4 SEPTEMBER 1970
GEORGIA INSTITUTE OF TECHNOLOGY

AGENDA

Thursday
3 September 1970

0900-0920	REGISTRATION	
0920	Welcome - Host	
0930	Welcome - AFOSR	
0940	Kinetic Cross Sections for Electron-Atom and Electron Molecule Collisions	H. H. Michels United Aircraft Research Laboratories
1010	Intermolecular Potential Energies by a Molecular Beam Scattering Method	E. W. Rothe Wayne State University
1040	COFFEE BREAK	
1100	Chemical Reactions by Crossed Beams	G. G. Volpi Universita di Perugia
1130	Properties of Energetic Ions Trapped in Solids: Photoconductivity in γ -Irradiated Alkaline Ice	L. Kevan Wayne State University
1200	Nonequilibrium Combustion Products	R. F. Sawyer University of California (Berkeley)
1230	LUNCH	
1345	Combustion Kinetics of Tetrafluoroethylene	R. A. Matula Drexel University
1415	Decomposition Kinetics of the Rocket Oxidizer Ammonium Perchlorate	E. E. Petersen University of California (Berkeley)

AGENDA

Thursday
3 September 1970

1445	The Kinetics of the Thermal Decomposition of F_2O	H. J. Schumacher Consejo Nacional de Investigaciones LaPlata, Argentina
1515	COFFEE BREAK	
1530	Kinetics of Fluorine Compounds	T. Houser Western Michigan University
1600	Chemical Kinetics of Fluorine Combustion Systems	D. I. MacLean Boston College
1630	Chemical Kinetics of Selected Fluorine Reactions	J. B. Levy George Washington University
1930	DINNER	

Friday
4 September 1970

0900	Vibrational Relaxation of CO_2 with Selected Collision Partners	D. J. Seery United Aircraft Research Labora- tories
0930	Laser-Induced Fluorescence of Metal Oxides	H. P. Broida University of California (Santa Barbara)
1000	Energy Migration in Irradiated Solids	J. Cunningham University College of Dublin
1030	COFFEE BREAK	
1100	Use of O^{17} Tracer Techniques in Studying the Chemistry of Various Oxidizers	I. Solomon IITRI

AGENDA

Friday
4 September 1970

1130	Synthesis, Stability and Energetics of High Energy Rocket Propellant Ingredients at Cryogenic Temperatures	H. A. McGee, Jr. Georgia Institute of Technology
1200	Photochemistry of Interhalogens	A. E. Axworthy Rocketdyne Divi- sion North Ameri- can Rockwell
1230	LUNCH	
1345	Interfacial Chemical Reactions	D. E. Rosner Yale University
1415	Oxidation Reaction Studies of the Paraffin Hydrocarbons	I. Glassman Princeton Univer- sity
1445	The Oxidation of Methyl Radicals	R. R. Baldwin University of Hull
1515	Studies of Excited Hydrogen in Relation to Advanced Propulsion	J. M. Flournoy Tetra Tech
1545	ADJOURN	

KINETIC CROSS SECTIONS FOR ELECTRON-ATOM
AND ELECTRON-MOLECULE COLLISIONS^a

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Practical computational techniques are under development for calculating the kinetic cross sections for collisions between electrons, neutral atoms and molecules. The initial phases of this investigation were directed toward the development of analytic methods useful for describing both elastic and inelastic electron-atom collisions. A non-arbitrary (minimum norm) method was formulated¹ and a computer program for implementing this method is now in the final check-out stage. Part of this year's effort was devoted to the development of accurate and efficient procedures for evaluating the integrals needed for expansion calculations of electron-atom scattering.² Preliminary results have been obtained for e-H, and e-He and e-O. Further studies will involve an analysis of the accuracy of this minimum norm technique in comparison with other analytic expansions for the scattering wavefunction and with close-coupling numerical results.

Some studies of collisional excitation of molecules by electron impact have been initiated this past year. In particular, we have begun

^a Project AF-AFOSR-AF49 (638)-1711.

¹ F. E. Harris & H. H. Michels, Phys. Rev. Letters 22, 1036 (1969).

² F. E. Harris & H. H. Michels, J. Comp. Phys. 4, 579 (1969).

an analysis of the photo- and collisional detachment of electrons from O_2^- . The dominant features of the cross section for this reaction are connected with the Franck-Condon transition probabilities between the ground $^2\Pi_g$ state of O_2^- and excited vibrational states of O_2 . Ab initio studies are now in progress to determine the electronic structure and properties of O_2^- in order to assess the strength of these molecular transitions. In addition, a preliminary study of dissociative-recombination reactions has been undertaken. A model has been developed which should permit calculation of the temperature dependence of the product distribution for these reactions. This information is normally not available from experiments but is needed for a more complete understanding of the kinetics governing the relaxation of high-temperature gases. Future studies will involve detailed calculations with this kinetic model.

INTERMOLECULAR POTENTIAL ENERGIES BY A MOLECULAR BEAM
SCATTERING METHOD^{*}

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Last summer we moved the molecular beam apparatus from San Diego to Detroit and, after an induction period, started anew. Accordingly, two types of work are discussed: a) experiments done in San Diego, but whose analysis was done here and b) experiments performed here.

The San Diego experiments were intermolecular potential-energy determinations using glory-scattering from polyatomics. These have now been analyzed, and three papers will appear soon. In two of these we describe the experiments,¹ and in the other we formulate a theoretical framework.³

The experiments in Detroit are planned to investigate ionizing "harpoon-type" collisions of neutrals, in the energy range of 1-50 eV. We previously published the results of a preliminary study.⁴ Because we had a deadline for moving the laboratory, some "stop-gap" measures were required to complete a basic measurement. These improvisations⁵ did this job well, but their use precluded the observation of other phenomena that would have been very interesting. We are now working with a more versatile experimental arrangement.

* Grant AFOSR 69-1799

Grant AFOSR 69-1799

Page 2.

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2. E.W. Rothe and R.K.B. Helbing, J. Chem. Phys. 53, (scheduled for September 15, 1970 issue).
3. R.K.B. Helbing, J. Chem. Phys. 53, (scheduled for August 1, 1970 issue).
4. R.K.B. Helbing and E.W. Rothe, J. Chem. Phys. 51, 1607 (1969).
5. "There is one scientist renowned for his masterful improvisations, but some think even he went too far when he published that he had cleaned out his apparatus by pushing a cat through it !", from E. Bright Wilson, Jr., An Introduction to Scientific Research (McGraw-Hill, New York 1952) p. 72.

Chemical Reactions by Crossed Beams*

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(Italy)

As an approach toward the investigation of reactive collisions, which requires both the overcoming of experimental intensity problems and the understanding of the dynamics of elastic and inelastic collisions, two apparatuses are presently being used at the University of Perugia. The first one is designed for the study of elastic scattering between atoms and simple molecules, under conditions of velocity selected atomic beams. Studies of collisions of rare gas atoms with several molecules are under way; they give information about the intermolecular forces pertinent to these systems. An intense atomic hydrogen beam source has also been developed, and will be used in the near future.

The second apparatus unites the technique of crossed beams to the spectroscopic observation of the emission of excited species produced by the collision. In particular, an alkali ion beam is crossed with an alkali atom beam at energies variable in the range from a few eV to a few KeV. The electronic excitation from the conversion of energy from traslational to internal is measured by optical methods.

*

Work sponsored in part under Contract EOAR F61052-68-C-0068, presented at the 11th AFOSR Meeting on Kinetic of Energy Conversion, September 3 and 4, 1970, Atlanta, Ga.

PROPERTIES OF ENERGETIC IONS TRAPPED IN
SOLIDS: PHOTOCONDUCTIVITY IN γ -IRRADIATED
ALKALINE ICE

Project AF-AFOSR-70-1852A

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ABSTRACT

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 this study optical excitation leading to photoconduction is examined. Electrons produced by γ -irradiation can be trapped with 80-90% efficiency in glassy alkaline ice (10 M NaOH) at 77°K. These trapped electrons are characterized by EPR and optical absorption spectra. Bleaching in the optical band produces photoconduction. The photocurrent shows no activated temperature dependence between 4° and 77°K and under certain conditions to 120°K, and the wavelength dependence of the photocurrent coincides with the absorption band. These results show that no stable bound excited state exists for the trapped electron in the polar alkaline ice matrix. The relation of this result to the importance of short range interactions in electron binding is discussed. Detailed studies of photoconduction at temperatures above 90°K show that radiation-produced shallow traps for electrons are formed. These traps have an average depth of 0.048 eV and appear to be associated with a lattice distortion created by the presence of O^- . Both ohmic and superohmic currents are found under certain conditions. The superohmic current is interpreted as due to a voltage dependent lifetime of conduction band electrons.

NONEQUILIBRIUM COMBUSTION PRODUCTS^a

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M. C. Branch, Research Assistant

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Department of Mechanical Engineering
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The identification of nonequilibrium combustion products, the nature of their chemical kinetics, and their effect on propellant performance have been objectives of this investigation. Earlier work has focused upon (1) the identification of nonequilibrium combustion products based upon rocket combustor studies at the Air Force Rocket Propulsion Laboratory, (2) the mathematical modeling of simplified gas phase combustion processes and the numerical techniques for the solution of these models, and (3) the prediction of the effect of nonequilibrium combustion products upon propellant performance.

The development of a flow reactor technique for extracting global rate data through point sampling was undertaken. Initial, demonstration experiments on methane oxidation were conducted in a moderate temperature (to 1300°K) flow reactor. Sample collection was through a water cooled, aerodynamic quenching probe with low pressure transfer to a time-of-flight mass spectrometer. Statistical data analysis techniques for rate calculations and the systematic extraction of concentration dependency (orders), temperature dependency (overall activation energy), and rate constants have been developed.

^aProject AF-AFOSR-1256-67

A high temperature flow reactor is being developed which allows for the addition of a reactant gas to an argon stream heated by a 75 kw plasma arc. The heated argon, at a bulk temperature of 2500-3000°K flows through a water cooled plenum chamber where diluent argon is added and relaxation of electronically excited state is facilitated. The gas stream then converges through a water cooled, stainless steel nozzle into a section for addition of reactant gas at from 1 to 10 percent of the bulk argon flow. The high velocity reactant stream enters the argon stream radially to promote turbulent mixing and uniform radial temperature and composition profiles. The mixed gas stream then flows through a zirconia reactor duct of inner diameter 3.17 cm and at a bulk temperature between 1600 and 2100°K. Regulation of argon flow rate provides control of flow velocity and hence reaction time scale. Gas temperature is controlled by the power to the plasma arc.

A Grehrad model G-13 calorimetric sampling probe will be used for simultaneous sample extraction and gas temperature determination. The sampled gas is analyzed with a Bendix time-of-flight mass spectrometer. Operation of the flow reactor is in the turbulent regime at atmospheric pressure. The overall reactor length of 45 cm and flow velocities up to 100 m/sec give reaction times in the millisecond range.

The kinetic interpretation of reacting systems containing nitrogen and hydrogen is hampered by the lack of experimental data on homogeneous decomposition of ammonia. This problem relates directly to the performance of hydrazine, both as a monopropellant and as a fuel in combination with an oxidizer. The overall reaction kinetics of the thermal decomposition of ammonia is planned as the initial study using the high temperature flow reactor.

COMBUSTION KINETICS OF TETRAFLUOROETHYLENE^a

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The thermal dissociation of carbonyl fluoride (CF_2O) in excess argon, $\text{CF}_2\text{O} \xrightarrow{\Delta} \text{CFO} + \text{F}$, was studied behind both incident and reflected shock waves. Preliminary kinetic data have been obtained in the temperature and total pressure ranges 2500-3200°K and 0.5-14 atmospheres. Dissociation rates of carbonyl fluoride were followed by monitoring infrared emission from its 5.15 micron fundamental band, and the effect of optical depth on kinetic measurements is discussed. The reaction was found to be unimolecular, and the pressure and temperature dependence of the CF_2O dissociation rate constant were analyzed by both the Lindemann and the Rice-Ramsperger-Kassel unimolecular theory of reaction rates. The high pressure rate constant was found to be represented by

$$k_{\infty} = (9.66 \pm 0.09) \times 10^{10} \exp \left(- \frac{91912}{R_u T} \right) \text{ sec}^{-1}$$

and the pressure dependence of the observed rate constant was found to be given by

$$k_{\text{obs}} = 8.05 \times 10^8 \exp \left(- \frac{46257}{T} \right) \int_0^{\infty} \frac{x^5 e^{-x} dx}{1 + \frac{282.18 T^{1/2}}{P} \left(\frac{x}{\frac{46257}{T} + x} \right)^5}$$

where T is in °K and P is in atmospheres. These preliminary results are compared to the results of previous investigators.

The spectral absorption coefficient and integrated intensity of the 1942 cm^{-1} fundamental band of CF_2O as a function of pressure and temperature has been studied during the past year. The experimental data have been obtained in the pressure and temperature

^a

Grant AF-AFOSR-68-1606D

ranges 1 to 760 torr and 300 to 650K respectively. Since CF_2O can be well represented as an oblate symmetric top molecule, theoretical expressions for energy level populations and transition moments can be obtained, and hence the dependence of spectral absorption coefficient on wave number can be predicted. A computer program has been developed to predict the spectral absorption coefficient versus wave number and temperature for the CF_2O fundamental. If account is taken of the fact that the 1942 cm^{-1} band is overlapped by a moderately weak overtone band at 1907 cm^{-1} and a very weak combination band at 2010 cm^{-1} , the theoretical and experimental values can be compared.

In the temperature range of 300 to 650°K, comparison between theory and experiment is excellent, and hence the theoretical model can be used to evaluate the spectral absorption coefficient of the 1942 cm^{-1} band versus wave number at temperatures of interest in fluorocarbon combustion studies.

DECOMPOSITION KINETICS OF THE ROCKET OXIDIZER AMMONIUM PERCHLORATE^a

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Department of Chemical Engineering
University of California, Berkeley

Ammonium perchlorate (AP) is one of the most common oxidizers used in solid propellants; yet relatively little can be agreed upon concerning the controlling mechanism in solid propellant combustion. In such a propellant powdered AP is mixed with fuel, catalyst, and plasticizer, all of which severely complicate the description of the burning process; hence a simpler system was sought for a more fundamental study. In light of these experimental considerations, large single crystals of pure and doped AP have been grown from saturated aqueous solution and were used in this study of AP deflagration and deflagration limits.

Deflagration experiments at low and high ambient single crystal temperatures has emphasized the effects on burning behavior of AP due to addition of small amounts of catalyst. These experiments suggest the desirability of studying the effect of catalysts and catalyst compositions in order to control the deflagration and deflagration limits of oxidizers in propellant formulations. Such data also may be useful in the future for writing specifications on AP used in propellants.

An accurate technique for studying deflagration and deflagration limits has been developed. By imposing a temperature

^aProject AF-AFOSR - 68 - 1458.

gradient on a single crystal or pellet and arranging the lowest temperature to a value below the deflagration limit, the crystal extinguishes during the process. This simple concept has permitted the accurate determination of the deflagration pressure limits as a function of ambient crystal temperatures by a quenching experiment. Therefore, the measurements are no longer dependent upon the magnitude of the ignition stimulus strength as was true for previous measurements. This technique may be utilized to study pure and doped crystals.

The deflagration limit data above provide an opportunity to test a unified theory of ignition and deflagration because at the low pressure deflagration limit the ignition process coincides with the deflagration process. Accordingly a unified theory of ignition and deflagration using these data is nearly complete which predicts the magnitude of the deflagration limit. Also the theory is the most effective way of ascertaining information on the effects of catalysts on the deflagration process.

THE KINETICS OF THE THERMAL DECOMPOSITION OF F_2O

by
J. Czarnowski and H. J. Schumacher

The kinetics of F_2O decomposition was reinvestigated in a static system between 230 and 310°C and a pressure range from 10 to 750 torr using vessels of Mg, Al or quartz (up to 290°C). The "mixing" and "inlet" time of the gases was of the order of 10 sec.

No induction period could be observed. All added gases increased the rate of decomposition. Comparing equal pressures, the efficiencies of F_2 and He were almost the same.

For the heat of activation a value of $36,9 \pm 0,5$ kcal was obtained.

The second order constants corresponding to the decomposition of pure F_2O showed a small trend to decrease with increasing pressure. Experiments in vessels with great v/s values will be made in order to prove if this effect is real and belongs to the homogenous reaction.

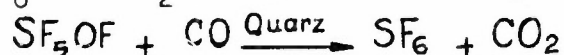
A series of experiments was executed to find out, if the bimolecular reaction between $2OF$ radicals leads directly to the formation of F_2 and O_2 or to the formation of O_2 and $2F$. However, we could not yet come to a finite conclusion.

- - - - -

THE KINETICS OF THE THERMAL REACTION BETWEEN SF_5OF and CO

by
A. J. Colussi and H. J. Schumacher

The reaction between SF_5OF and CO was investigated in a quartz vessel between 110° and 150°C. It is a homogenous chain reaction, SF_6 and CO_2 being formed in equimolecular amounts.

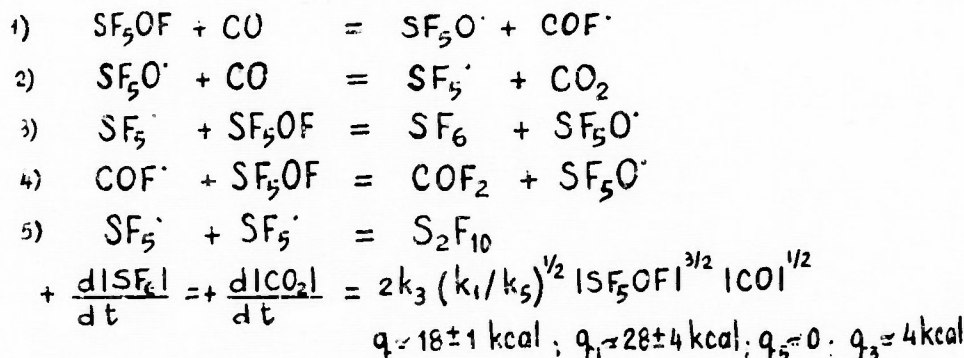


The rate follows the equation

$$+ \frac{d[\text{SF}_6]}{dt} = k [\text{SF}_5\text{OF}]^{3/2} [\text{CO}]^{1/2}$$

Oxygen inhibits the reaction.

The results can be explained by the following mechanism:



In reactors of Cu and Ni the reaction is heterogenous, leading in agreement with Gady to the formation of SOCl_4 and COF_2 .

- - - - -

THE PHOTOCHEMICAL FORMATION OF ClF_3 IN THE SYSTEM $\text{F}_2 + \text{ClF}$

by
E.A. San Román and H.J. Schumacher

The reaction between F_2 and ClF in light of 365mμ has been investigated between 30 and 50°C. If the excess of F_2 over ClF is sufficiently high, $\text{F}_2/\text{FCI} > 2$, the quantum efficiency, Φ , of ClF_3 formation is 1.0 Mol/hν. Under this condition Φ is independent of temperature, pressure and the presence of oxygen. It furthermore does not matter, if the light is absorbed by F_2 or ClF .

A mechanism, which explains the results, is given.

KINETICS OF FLUORINE COMPOUNDS^a

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The kinetics of the pyrolysis of OF_2 has been studied using a monel, stirred-flow reactor. The experimental conditions employed in the study were: temperatures of 330 to 430°C, one atmosphere total pressure, and 1 to 10 mole per cent initial concentration of OF_2 with He as the diluent. Under these conditions the unimolecular steps in the reaction would be in the second-order pressure region with most of the collision activation coming from the He; this results in these unimolecular steps appearing to be first-order since the total pressure does not change during reaction.

It was found that at temperatures 330 to 385°C the rate was definitely lower than first-order with respect to initial concentration and about first-order with respect to time. At 407 and 430°C the rate was about first-order with respect to initial concentration and appeared to be less than first-order with respect to time. The addition of F_2 produced a small inhibition of the rate. Increasing the surface area of the reactor by about a factor of 2.5 changed the rate by only about 10% and did not change the apparent order of the reaction. It was concluded that the reaction was primarily homogeneous and that the observed low order did not result from heterogeneity.

Based on the above observations, an equation of the following form appeared reasonable for the initial rates.

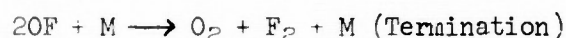
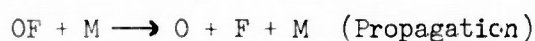
$$r_0 = k(\text{OF}_2)_0 + k(\text{OF}_2)_0^{1/2}$$

^aProject AF-AFOSR-1291-67

The change in order with respect to concentration with temperature could be explained by the shift in relative size of the two terms. Values of the first-order rate constant are described by the equation

$$k = 10^{10.5} \exp(-34,000/RT) \text{sec}^{-1}$$

A mechanism, the steady-state treatment of which produces a 1/2 order term in OF_2 and an overall total pressure order of less than two, involves the following steps:



It is realized that other propagation-termination steps are reasonable and probably contribute to the reaction; however, the observed order is strong evidence that the above steps are significant contributors to the overall complex mechanism.

It is planned to study the rate of the reaction



using microwave discharge as a source of F atoms.

The kinetics of the H_2 - OF_2 reaction have been studied in the same system over a temperature range of 110-220°C. The reaction's stoichiometry is



The rate was strongly inhibited by O_2 . Experimental variation of OF_2 , H_2 and O_2 concentrations leads to a rate expression of the form

$$r = k_a(\text{OF}_2) + k_b(\text{OF}_2)(\text{H}_2)^m + \frac{k_c(\text{OF}_2)(\text{H}_2)^n}{1 + b(\text{O}_2)/(\text{OF}_2)}$$

where m and n could be 1 or 1/2. The first term represents the heterogeneous contribution to the rate.

Work is continuing to better define the terms in the rate equation.

CHEMICAL KINETICS OF FLUORINE COMBUSTION SYSTEMS^a

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ABSTRACT

Reactions of the systems $\text{H}_2 + \text{F}_2$, $\text{NH}_3 + \text{F}_2$ and $\text{C}_2\text{H}_2 + \text{F}_2$ have been studied in low pressure diffusion flames by means of visible-ultraviolet spectroscopy and time-of-flight mass spectrometry. Two types of multidiffusion burners were developed, the one employing fine copper capillaries arranged in a 3 cm diameter circle, and the other aluminum slits in a 5 x 5 cm array. A differentially pumped molecular beam sampling system was constructed for the mass spectrometer.

Concentration profiles have been measured for $\text{H}_2 + \text{F}_2$ flames diluted with Argon, burning at a pressure of 6 mm Hg on a multidiffusion burner. Under these conditions the flame is hypergolic. For a mixture containing 27% F_2 and 19.5% H_2 at an overall flow rate of 41.2 cc/sec (at 1 atm. and room temperature) a faint red glow is observed in the oxidation zone of the flame but not in the burned gases. The main reaction zone is about 8 mm thick. Fluorine atoms are detectable in the second half of the reaction zone; their concentration increases steadily into the burned gas, peaking at about 15 mm above the burner. Under these conditions of excess F_2 in the flame, H-atoms were too low in concentration to be detected, due to the fast reaction $\text{H} + \text{F}_2$. The flame goes out below 13% ($\text{H}_2 + \text{F}_2$) in Argon at 10 torr pressure.

Although the $\text{NH}_3 + \text{F}_2$ system is hypergolic at atmospheric pressure, it was not possible to ignite it at several centimeters Hg. The flame was finally ignited by substitution of H_2 with NH_3 in an H_2 - F_2 flame. The flame velocity of NH_3 - F_2 is substantially lower than that of H_2 - F_2 ; also a certain in-

hibitory effect of NH_3 on $\text{H}_2\text{-F}_2$ flames was observed. At 2-3 torr the flame is dark green, at 6-10 torr yellow-green with a purple rim at the top of the combustion zone. The main products of this flame are N_2 and HF . As intermediates NH_2F and NHF_2 are formed, and in smaller amounts also NF_3 . Furthermore the presence of N_2F_2 , N_2H_2 , NF_2 , NH_2 and NH radicals has been determined. Hydrazine could not be detected as an intermediate.

Of interest for the study of fluorine reactions at high temperature is the system acetylene-fluorine because of the high exothermicity of the reaction and the consequent high flame temperature.

The main reaction zone, appearing blue to the eye, has a thickness of about 5 mm at a pressure of 5 mm Hg. The total initial flow was 18 cc/sec at 1 atm, with an initial $\text{F}_2/\text{C}_2\text{H}_2$ ratio of 3.5. The main reaction products are CF_2 and HF , with less than 10 mole percent CF_4 being formed. Of particular interest is the large concentration of the radical CF_2 in the burned gas, since this could be used for the study of some reactions of this active species. Intermediate radicals for which only qualitative profiles have been measured as yet are CF_3 and CF . Furthermore, a number of partially fluorinated unsaturated hydrocarbons are formed in the main reaction zone but disappear again in the burned gas. Among these are C_2HF , C_4HF and $\text{C}_2\text{H}_2\text{F}_2$. Also observed is C_4H_2 which is known to be formed in $\text{C}_2\text{H}_2\text{-O}_2$ flames. C_2F_2 is also formed but in comparatively low concentration. No higher fluoro compounds than C_2F_2 could be detected.

Plans for the future include the measurement of temperature profiles for these flames and study of their stability limits. Other fluorine-containing systems will also be investigated in flames and shock fronts.

^aProject AF-AFOSR 68-1523

CHEMICAL KINETICS OF SELECTED FLUORINE REACTIONS (1)

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This program has begun as of September 1, 1970. Its goal is to add to our knowledge of the chemistry of fluorine and its compounds by investigating the kinetics of some chemically-simple systems.

The systems of chief interest are fluorine-chlorine, fluorine-chlorine monofluoride and fluorine-xenon. The first has been studied thermally to some extent (2, 3) and appears to be a chain reaction yielding mainly chlorine monofluoride. In this program the plan is to study the photochemical system in order to evaluate more carefully the energetics of the chain-propagation steps. The effect of oxygen on the system will also be studied to try to learn more about the ClOO and FOO species. The second system, which has not been studied to date, will also be examined photochemically.

It is known that xenon and fluorine react photochemically to give xenon difluoride at room temperature (4). The reaction kinetics of this system will be studied to learn about the energetics of reactions of fluorine atoms with xenon and xenon fluoride species (5, 6).

(1) AFOSR Grant No. 70-1939

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(3) E. A. Fletcher and B. E. Dakneke, *J. Am. Chem. Soc.*, 91, 1603 (1969).

(4) J. L. Weeks, C. L. Chernick and M. S. Matheson, *J. Am. Chem. Soc.*, 84, 4612 (1962).

(5) J. H. Holloway, *Progress in Inorganic Chemistry*, ed. by F. A. Cotton,

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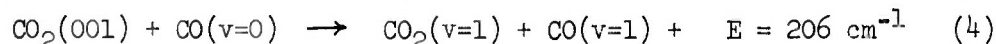
VIBRATIONAL RELAXATION OF CO₂ WITH
SELECTED COLLISION PARTNERS*

Daniel J. Seery

United Aircraft Research Laboratories
East Hartford, Connecticut 06108

The vibrational relaxation times of CO-CO₂ mixtures have been measured as a function of temperature. In addition, the experimental data have been further analyzed to obtain the rate of vibration-vibration energy transfer between CO₂(001) and CO(v=1).

The experimental technique consists of time-resolved measurements of the infrared from CO₂ at 4.3 μ and CO at 4.7 μ following shock-heating of the gas mixture. The exponential time constant for the growth of the emission signal is then related to the vibrational relaxation time of the mixture. In addition, the emission intensity profile of the CO at 4.7 μ can be used to calculate the rate of energy transfer between CO₂(001) and CO(v=1). The following reactions must be considered



Using literature values for the rates of (1), (2) and (3), the rate of reaction (4) can be calculated.

*Project AF-OSR-F44620-69-0100

Results of experiments and analysis on reaction (4) will be presented along with some new results on reaction (2). In addition, some work on HCl-CO₂ vibrational relaxation will be presented.

LASER-INDUCED FLUORESCENCE OF METAL OXIDES^a

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Fluorescence of BaO, MgO and PbO, excited by several lines of Ar⁺ laser and by a tunable dye laser pumped with a pulsed nitrogen laser, has been observed and spectra obtained between 400 and 1100 nm. Metal oxide molecules were produced at low pressures by gas phase chemical reactions at room temperature between metal vapors in an inert gas bath and both molecular and atom oxygen. Weak chemiluminescence was observed from BaO and PbO.

The A ¹Σ - X ¹Σ system of BaO has been most fully studied. Strongest fluorescence using seven Ar⁺ laser lines was observed from v' = 8, j' = 49 excited by 488.0 nm and v' = 7, j' = 3 and 7 excited by 496.5 nm. Transitions from v' = 1-12 in the upper electronic state to v'' = 0-17 in the ground state have been carefully measured, and rotational and vibrational constants for the lower electronic state have been obtained. Comparisons between measured intensities and calculated Franck-Condon factors have been made. A rotational perturbation in v' = 7 of the A ¹Σ state was found. Studies also were made of collisional energy transfer by varying pressure from 0.4 to 40 Torr giving cross sections for electronic quenching and for vibrational and rotational transfer by He of 0.25, 0.1 and 2 Å² respectively. Lifetime and quenching measurements using the tunable

^a Project AF-AFOSR-70-1851

dye laser are being made for $v' = 0-11$ of the A state. Present results show that for $v' = 0$, $\tau = (3.8 \pm 0.4) 10^{-7}$ sec and $\sigma_{el} = 0.1 \text{ \AA}^2$.

Strong fluorescence of MgO is observed with excitation by several Ar^+ lines but particle formation is extremely rapid causing a difficult problem of scattered light. The vibrational spacings of the series excited by 488 nm fits rather well with the first (known) excited state, $A^1\Pi$, but this identification is still uncertain.

Preliminary results using the tunable dye laser for the lifetimes of the $v' = 0, 1$ and 3 vibrational levels of the B state of PbO indicate $\tau \approx 1 \times 10^{-6}$ sec. Although PbO chemiluminescence is readily observed, fluorescence of PbO was not observed with the Ar^+ laser. However there is strong fluorescence from Pb_2 . Measurements indicate that ground state vibrational constants of Pb_2 are poorly known, and therefore new values of ω_e , $\omega_e x_e$, and the dissociation energy will be determined.

Title: ENERGY MIGRATION IN IRRADIATED SOLIDS

Project

Director: Dr. Joseph Cunningham

Address: Chemistry Department, University College, Dublin 4, Ireland.

Our Research in University College Dublin on Energy Transport in Irradiated Solids relates to the theme of this meeting on Kinetics of Energy Conversion mainly through our attempts to clarify basic steps in radiation-catalysed processes. Such processes aim to convert the energy of high-energy ionizing radiations into useful chemical potential by the sequence: (i) energy deposition into the solid catalyst, (ii) localization of energy at the catalyst surface (iii) catalysis of endothermic reaction at surface sites thus activated by radiation. If this sequence is to convert radiation energy with significant efficiency into chemical potential, necessary preconditions are (A) that transport of energy to the surface from its site of deposition be efficient and (B) that energy-transfer from the surface to adsorbed reactant molecules also be efficient. In our studies the efficiencies and kinetics of energy transfer processes type A and type B have been explored in model systems.

Type B energy-transfer is conveniently studied at the surfaces of n-type semiconductors illuminated with ultraviolet light, since energy is thereby deposited close to the surface. Gaseous reagents present at the illuminated surfaces signal transfer of energy either by photo desorbing from the surface, or by undergoing photo-assisted reactions. Nitrous oxide present above illuminated zinc oxides or ferric oxide undergoes additional photo assisted dissociation producing gaseous nitrogen and adsorbed oxygen. Ethylene or

* Project AF-AFOSR - 61052-67-C-O '4.

ethyl iodide present over illuminated ferric oxide photo desorbs but does not change chemically. Ethyl iodide present over illuminated zinc oxides yields several products. Quantum efficiencies of the photo assisted reactions are very low for these reactions involving reactants adsorbed from the gas phase. The low efficiencies and nature of products observed can be understood in terms of a rate determining step involving transfer of electrons from the bulk to the surface.

Much larger quantum efficiencies are observed for some photo-assisted reactions in aqueous solutions containing suspensions of zinc oxides. High yields are observed for photo oxidations which involve reaction with a hole rather than with an electron at the semiconductor surface. The possibility that excitons, produced by electron-hole recombination, contribute appreciably to the reaction at the surface is being investigated by comparing efficiencies of photo assisted reactions for species having absorption bands to longer wavelength (e.g. PNDA, riboflavin, KMnO_4) than the ZnO band edge with efficiency for species having absorption at shorter wavelengths (e.g. NO_3^- , NO_2^- , $\text{SO}_4^{=}$).

Type A energy transport is being investigated by incorporating radioactive nickel-63 ion into the zeolitic framework of molecular sieve type materials by ion exchange techniques. Of all the radiation energy deposited within these solids by β -rays of average energy 18 KeV, a fraction F_d can interact directly with surface sites, and a further fraction F_t may activate surface sites if transported to the surface from points of deposition within the solid. Various techniques have been employed without as yet obtaining evidence that F_t can be appreciable for these molecular sieve type materials. ESR techniques are being utilised in attempts to "count" the number of electrons which reach the surfaces of the sieves.

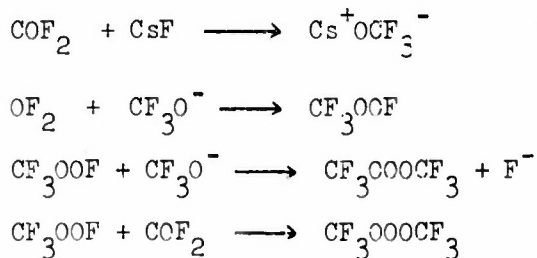
THE USE OF O^{17} TRACER TECHNIQUES IN STUDYING
THE CHEMISTRY OF VARIOUS OXIDIZERS^a

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The chemistry and properties of various nitrogen oxides are being studied by using oxygen-17 tracer techniques along with NMR and EPR studies. The following compounds have been prepared: NO^{17} , N_2O^{17} , $N_2O_3^{17}$, $N_2O_4^{17}$, and $N_2O_5^{17}$. The method of preparation of these compounds required specialized techniques, which will be discussed, due to the high cost of oxygen-17. The NMR and EPR work to be carried out will also be discussed.

Oxygen difluoride has been shown to react with carbonyl fluoride over a cesium fluoride catalyst to yield bis(trifluoromethyl) trioxide. It was postulated that this reaction occurs by the following mechanism:



Oxygen-17 tracer experiments have been carried out and are consistent with this mechanism. The reaction was then run in a way to favor the preparation and isolation of CF_3OOF . Although CF_3OOCF_3 , $CF_3CF_2CF_2OOF$, and $(CF_3)_2CFOOF$ have been reported the methods for their preparation are tedious. A convenient method of preparation CF_3OOF is discussed, as well as the generality of the preparative scheme.

^aProject F44620-70-C-0027

Submerged arc, exploding wire, and rf discharge techniques all failed to produce any evidence for chemical combination of He, Ne, or Ar with a wide variety of likely reagents.

Borane, BH_3 , was produced in reasonable yield from the pyrolysis of BH_3CO at 280° to 350° . The species survives a rapid quench to 67°K and subsequent revaporization. Mass spectrometric characterization was performed at 65° to 77°K , which revealed that the species unfortunately dimerises at temperatures where it exerts a vapor pressure of only 10^{-5} torr. Thus any practical utility of BH_3 seems unlikely. The new MINDO molecular orbital approximations were adapted to the family of B-H-F compounds with excellent results in predicting energetic quantities.

Aminoborane, H_2BNH_2 , the isoelectronic analog of ethylene has been produced from an rf discharge in borazine and rapid quench procedure. This highly reactive compound, unknown until now, has been isolated and energetically characterized at cryogenic temperatures. The species reacts with itself between -196° and -155°C to yield a very inert, white polymer. The chemistry of H_2BNH_2 is now being investigated.

One may postulate a wide variety of high energy species, but before embarking upon experimental synthesis programs, it would be informative to examine any theoretical guidelines that might be developed. Assuming a low activation energy, a relatively loose activated complex structure, a statistical dynamical model, and the INDO molecular orbital approximations, it has been possible to evaluate the activation energy and the reaction characteristics of several cryogenic reactions. The results, for example, on the CF_3 and BH_3 dimerizations seem reasonable. Further development of these notions are underway.

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PHOTOCHEMISTRY OF INTERHALOGENS^a

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A number of photochemical reactions involving interhalogens will be investigated during this program. These will include:



Kinetic studies of these photochemical reactions have not been reported previously.

The stainless steel reactor to be employed in these studies is equipped with sapphire windows. These materials are compatible with the halogens and interhalogens. Whenever possible, wavelengths will be used which will permit the primary photochemical process to be controlled.

During the course of the program, the photochemical mechanisms for reactions 1, 2, and 3 will be compared with the thermal reaction mechanisms reported in the literature for reactions 1 and 3, and with the mechanisms previously proposed for the thermal decomposition and photochemical formation of ClF_5 . Based on a proposed thermal mechanism, reaction 1 is expected to involve a long-chain. It is likely that reaction 2 (which is being investigated first) will proceed via the following chain mechanism:



^aProject AF-AFOSR - F44620-70-C-0094. This new program started 1 July 1970. Only the unclassified portions of the program will be discussed.

INTERFACIAL CHEMICAL REACTIONS^a

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This program is directed toward increasing our understanding of how transport and kinetic phenomena determine the rates of heterogeneous chemical and/or phase changes in systems of aerospace importance.¹ Recent theoretical studies are described in the following three areas:

- A. Bubble growth from supersaturated solutions.²
- B. Diffusion-limited dissolution of spheres in the absence³ or presence⁴ of homogeneous chemical reaction.
- C. Diffusion as a falsifier of heterogeneous kinetics in static and flow systems.

Additional theoretical work on the effects of homogeneous nucleation phenomena in boundary layers⁵ and mixing regions is currently in progress.

Our experimental apparatus for studying atom/solid reaction kinetics at temperatures up to the melting points of refractory solids⁶ has been reconstructed and improved at Yale University. Recent work on the O and N-atom attack of silicon carbide^{7,8} is reviewed. Future studies are outlined in the areas of: (i) new atom/solid systems of special interest, (ii) atom reactions on liquid surfaces, (iii) kinetics of gas dissolution in metals and (iv) oxide nucleation and aerosol production downstream of reacting filaments.

a Project AF-AFOSR-F44620-70-C-0026

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Oxidation Reaction Studies of the Paraffin Hydrocarbons

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Reported at the last contractual meeting were preliminary measurements of reactant-product concentration profiles for the methane/oxygen reaction in the turbulent flow reactor. Subsequent chemical profile data on this reaction and the propane/oxygen reaction has indicated that the simple thermal analysis used in previous investigations⁽¹⁾ is inadequate for predicting reactant concentration profiles for the paraffin hydrocarbon oxidations.

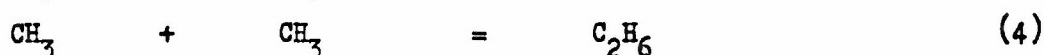
Review of alternative techniques has led to development of an experimental method using gas chromatography as the best procedure for making the type of absolute chemical measurements necessary for the established goals of the flow reactor program. Design of the new, advanced experimental system which uses cryogenic programming will be discussed in detail and some experimental reaction measurements recently taken will be reported.

THE OXIDATION OF METHYL RADICALS*

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Studies of the addition of CH_4 to slowly reacting mixtures of $\text{H}_2 + \text{O}_2$ have suggested that in a stoichiometric mixture, CH_3 radicals react predominantly with H_2 to reform CH_4 . To provide further information, the oxidation of CH_3CHO was examined in the temperature range $320^\circ - 540^\circ\text{C}$, a detailed study being made at 540°C . A surprising feature was the high yields of CH_4 (up to 60%) and of C_2H_6 (up to 8%), despite the thirty-fold excess of O_2 . These products are formed by the reactions:



and the ratio $k_3/k_4^{\frac{1}{2}}$ can be evaluated.

Over the range $440^\circ - 540^\circ\text{C}$, the yield of CH_4 rises from about 10% to 50%, with a corresponding decrease in the oxidation products. If the oxidation process is represented by the generalised reaction



the ratio k_{ox}/k_3 thus has a negative activation of about $30 \text{ kcal mole}^{-1}$.

Since $E_3 \approx 8 \text{ kcal mole}^{-1}$, $E_{\text{ox}} = -(20 \text{ to } 25) \text{ kcal mole}^{-1}$. This negative value rules out the direct bimolecular reaction (5) and can only be explained by using the termolecular reversible form (6).



* Contract AF EOOAR 68-0013

The oxidation of methyl radicals/continued

If the oxidation of CH_3O_2 occurs by the generalised process



then k_{ox} is given by:

$$k_{\text{ox}} = \frac{k_6 k_7 [\text{M}] [\text{X}]}{k_{-6} [\text{M}] + k_7 [\text{X}]}$$

If (-6) is the predominant reaction of CH_3O_2 radicals,

$k_{\text{ox}} = k_6 k_7 [\text{X}] / k_{-6}$. The high negative activation energy for k_{ox} is thus explained by the high value of E_{-6} compared to E_6 and E_7 .

Other reaction products include HCHO , CH_3OH and H_2 , and information on the mechanism of their formation, and on the nature of reaction (7), can be obtained by studying the effect of mixture composition on the reaction rate and on the yields of products.

STUDIES OF EXCITED HYDROGEN IN RELATION
TO ADVANCED PROPULSION^a

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Investigations in a flow system are continuing on the deactivation of vibrationally excited hydrogen by transfer of vibrational energy to other molecules and by collisions with various surfaces. High yields of vibrationally excited H_2 and D_2 are obtained when atoms formed in a microwave discharge combine on bare Pyrex or quartz. The excited molecules have been found to be very efficient for collisional excitation transfer to the C-H stretching mode of HCN. High resolution infrared emission spectra of the 3.0-micron band of HCN have been obtained in this manner (Ref. 1), and weaker infrared emissions from H_2O and CO_2 have also been observed.

Kinetic studies of chemical reactions involving vibrationally excited H_2 and D_2 are being undertaken but are currently limited by the presence of some residual atoms in the excited gas mixture. Efforts are being made to produce an atom-free stream containing significant concentrations of excited molecules.

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1. J.M. Flournoy and L.Y. Nelson, Chem. Phys. Letters, 6 (in press)

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13. ABSTRACT

This report consists of the agenda and abstracts of papers presented at the Eleventh Annual Contractor's Meeting on Kinetics of Energy Conversion held at the Georgia Institute of Technology, Atlanta, Georgia on 3-4 September 1970. The abstracts describe work now in progress under the sponsorship of the Energetics Division, Directorate of Aeromechanics and Energetics, 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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