ELEMENTARY RATE CONSTANTS FOR HYDROGEN ATOMS

1974-75

FINAL REPORT

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TABLE OF CONTENTS

FINAL REPORT, by Joe V. Michael

A. Introduction	1
B. Personnel	2
C. Facilities	2
D. Manuscripts Submitted for Publication	3
E. Publications	3
F. Manuscripts in Preparation	4
G. Theses	5
H. Acknowledgements.....	6

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I. FINAL REPORT

A. INTRODUCTION

This Final Report summarizes work done under Contract AT(11-1)-3242 (formerly AT(30-1)-3794) for the years 1966-1975. This is the ninth complete year for this contract. During this period the contract has supported the research of eleven workers including the principal investigator. Nine of these workers have successfully defended Ph.D. theses which have been submitted to the Department of Chemistry at Carnegie-Mellon University. They are Drs. J. R. Barker, D. T. Osborne, C. T. Yeh, G. N. Suess, D. G. Keil, J. J. Ahumada, T. C. Schwab, J. A. Cowfer, and K. P. Lynch. In addition, one student, Mr. S. D. Gleditsch, has been awarded an M.S. degree from Carnegie-Mellon University.

In past years this contract has supported the construction of and experimentation with six experimental apparatuses. This has included tuition and salary support of students. The principal purpose of the experimentation has been to develop techniques to measure the absolute rate constants for hydrogen atoms with various substrate reactions in the gas phase. The work has concentrated primarily on the pressure dependence of various reactions at room temperature.

As given in past years' Renewal Proposals and Annual Progress Reports, the contract has specifically supported the following projects: (A) A flow system experiment in which hydrogen atom concentration is monitored by Lyman- α photometry, (B) a real time apparatus which utilizes Lyman- α photometry to observe photolytically produced transient concentrations of hydrogen atoms in reacting systems, (C) a steady state photolytic system in which steady state hydrogen

atom concentration can be observed by Lyman- α photometry, (D) a shock tube experiment in which the high temperature reactions of transient hydrogen atoms may be studied by time resolved Lyman- α photometry, (E) a flow system experiment in which hydrogen atom and other neutral atom and molecule concentrations may be observed in reactive systems by time-of-flight mass spectrometry, (F) a steady state experiment where 2537 Å emission of $\text{Hg}(^3\text{P}_1)$ can be studied as a function of pressure of added quencher, and (G) theoretical calculations. All of the projects have been operational and have yielded data of interest to radiation chemists, photochemists, and chemical kinetics.

B. PERSONNEL

The principal investigator on this project has been Associate Professor Joe V. Michael of Carnegie-Mellon University. The Contract has supported thesis research of ten graduate students during its duration. These are:

Dr. John R. Barker, Stanford Research Institute, Menlo Park, CA.
 Dr. David T. Osborne, Inland Lighting, Baltimore, MD
 Dr. Chuin T. Yeh, National Tsing Hua University, Taiwan
 Dr. David G. Keil, University of Washington, Seattle, WA
 Dr. Gregory N. Suess, Center for Naval Analysis, Arlington, VA
 Dr. Jorge J. Ahumada, Federal Government, Colciencias, Bogota, Columbia
 Dr. Thomas C. Schwab, Engelhard Industries, Plainfield, NJ
 Dr. Joseph A. Cowfer, B. F. Goodrich Co., Brecksville, OH
 Dr. Kevin P. Lynch, Amoco Oil Co., Naperville, IL
 Mr. Scott D. Gleditsch, Hannemann Medical School, Philadelphia, PA

C. FACILITIES

The laboratories which housed this project are contained in the Mellon Institute building at Carnegie-Mellon University. The personnel working under this project have had access to a large variety of helpful resources and resource personnel which are invaluable for successful research. These have included excellent machinists, electronic technicians, glassblowers, instrument technicians, and computer technicians, each category having in turn excellent facilities designed for general research support. The project also has enjoyed the use of a large variety of general research instrumentation under the auspices of both

the instruments stockroom and the Chemistry Department of Carnegie-Mellon University. Secretaries, draftsmen, photographers, and printers have also been available to the project on a per job basis.

D. MANUSCRIPTS SUBMITTED FOR PUBLICATION

Diffusion of Hydrogen Atoms in Spherical Vessels, K. P. Lynch and J. V.

Michael, to Int. J. Chem. Kin.

E. PUBLICATIONS

An Experimental Estimate of the Oscillator Strength of the $^2P_{3/2,1/2} - ^2S_{1/2}$ Transition in the Hydrogen Atom, J. R. Barker and J. V. Michael, J. Opt. Soc. Am. 58, 1615 (1968).

Time Resolved Lyman- α Photometry in a Chemical Kinetic Investigation of $H + C_2H_4$, J. V. Michael and D. T. Osborne, Chem. Phys. Letters 3, 402 (1969).

The Reaction of Hydrogen Atoms with Ethylene, J. R. Barker and J. V. Michael, J. Chem. Phys. 51, 850 (1969).

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Absolute Cross Section for $Hg(^3P_1) + H_2$ and the Imprisonment Lifetimes for $Hg(^3P_1)$ at Low Opacity, J. V. Michael and C. Yeh, J. Chem. Phys. 53, 59 (1970).

Absolute Rate Constants for the Reactions of Hydrogen Atoms with Olefins, J. A. Cowfer, D. G. Keil, J. V. Michael, and C. Yeh, J. Phys. Chem. 75, 1584 (1971).

Pressure Dependence and Third Body Effects on the Rate Constants for $H + O_2$, $H + NO$, and $H + CO$, J. J. Ahumada, J. V. Michael, and D. T. Osborne, J. Chem. Phys. 57, 3736 (1972).

Reaction $H + C_2H_4$: Investigation into the Effects of Pressure, Stoichiometry, and the Nature of the Third Body Species, J. V. Michael, D. T. Osborne, and G. N. Suess, J. Chem. Phys. 58, 2800 (1973).

Application of RRKM Theory to the Chemical and Thermal Activation of Ethyl Radicals, J. V. Michael and G. N. Suess, J. Chem. Phys. 58, 2807 (1973).

The Chemical Kinetic Effects of Walls on Active Species: Results for Hydrogen Atoms, J. J. Ahumada and J. V. Michael, J. Phys. Chem. 78, 465 (1974).

Absolute Quenching Cross Sections of Hg ($3P_1$) with Various Molecules, J. V. Michael and G. N. Suess, J. Phys. Chem. 78, 482 (1974).

Further Hg ($3P_1$) Quenching Studies, S. D. Gleditsch and J. V. Michael, J. Phys. Chem. 79, 409 (1975).

An Investigation of Nonequilibrium Kinetic Isotope Effects in Chemically Activated Ethyl Radicals, J. A. Cowfer and J. V. Michael, J. Chem. Phys. 62, 3504 (1975).

Reactions of Hydrogen and Deuterium with Silane and Mono- Di-, and Trimethylsilanes at Room Temperature, J. A. Cowfer, K. P. Lynch and J. V. Michael, J. Phys. Chem. 79, 1139 (1975).

Lyman- α Absorption Photometry at High Pressure and Atom Density: Kinetic Results for H Recombination, K. P. Lynch, T. C. Schwab, and J. V. Michael, Int. J. Chem. Kin. 8, 651 (1976).

An Investigation of Nonequilibrium Kinetic Isotope Effects in Chemically Activated Vinyl Radicals, D. G. Keil, K. P. Lynch, J. A. Cowfer, and J. V. Michael, Int. J. Chem. Kin. 8, 825 (1976).

F. MANUSCRIPTS IN PREPARATION

A Mechanism for the Mercury Photosensitized Decomposition of Hydrogen, J. J. Ahumada, J. V. Michael, and C. Yeh.

G. THESES

I. Experimental Determination of the Oscillator Strength of the $^2P_{3/2,1/2} \leftarrow ^2S_{1/2}$ Transition of Atomic Hydrogen. II. Absolute Rate Constants for the Reactions $H + C_2H_4$ and $H + C_2D_4$. III. Steric Collision Theory of Reaction Rates: The Hydrogen Exchange Reactions, by John R. Barker

Absolute Rate Constants and Relative Third Body Effects for the Reactions: $H + C_2H_4$, $H + C_2D_4$, $D + C_2D_4$, $H + C_2H_2$, $H + O_2$, and $H + NO$, by David T. Osborne.

The Lyman α Photometric Measurements of the Steady-State Hydrogen Atom Concentrations from the Mercury Photosensitized Decomposition of Molecular Hydrogen. I. Primary and Secondary Photosensitization Process Studies. II. Rate Constants for $H +$ Various Unsaturated Hydrocarbons, by Chuin-tih Yeh.

An Investigation of Some Gas Phase Reactions of Hydrogen Atoms with Unsaturated Hydrocarbons and Some Isotopic and Mixed Isotopic Variations by Mass Spectrometric Detection in a Discharge Flow System: Absolute Rate Determinations and Mechanism Investigations, by David George Keil.

I. A Study of Stoichiometry and Pressure Effects in Experimental Rate Constants for the Reaction $H + C_2H_4$. II. Absolute Quenching Cross Sections of $Hg(^3P_1)$ with Various Molecules. III. A Study of Charge Contraction in Bonded Hydrogen Atoms from X-Ray Diffraction Data, by Gregory Neil Suess.

The Usefulness of the Mercury-Photosensitized Decomposition of Molecular Hydrogen as a Source of Hydrogen Atoms in Chemical Kinetics, by Jorge J. Ahumada.

A Kinetic Investigation of the Thermal Dissociation of Molecular Hydrogen in a Shock Tube using a Technique of Lyman- α Photometric Detection, by Thomas C. Schwab.

I. Experimental and Theoretical Investigation of Non-equilibrium Kinetic Isotope Effects in Chemically Activated Ethyl Radicals. II. A Kinetic Investigation of the Reactions of Atomic Hydrogen and Deuterium with Silane and Mono-, Di-, and Trimethylsilane Conducted in a Discharge Flow System with Mass Spectrometric Detection, by Joseph A. Cowfer.

I. Lyman- α Absorption Photometry at High Pressure and Atom Density:
Kinetic Results for Hydrogen Atom Recombination. II. Diffusion of Hydrogen
Atoms in Spherical Vessels. III. Application of RRKM Theory to Chemically
Activated Vinyl Radicals; by Kevin P. Lynch.

Quenching Cross Sections for Mercury (6^3P_1) with a Variety of Molecules,
by Scott D. Gleditsch.

H. ACKNOWLEDGEMENTS

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