ELEMENTARY RATE CONSTANTS FOR HYDROGEN ATOMS

1973-74

ANNUAL PROGRESS REPORT

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September 1, 1974

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PART I GENERAL REPORT

A. INTRODUCTION

This Annual Progress Report summarizes work done under Contract AT(11-1)-3242 for the year 1973-74. This is the eighth complete year for this contract and its predecessor, AT(30-1)-3794. In these eight years the contract has supported the entire research work of eleven workers including the principal investigator. Eight of these workers have submitted theses based on work done under this contract. Seven of these theses have been for the Ph.D. and one is for the M.S. Degree. These are:

Dr. John R. Barker; Stanford Research Institute, Menlo Park, Ca.

Dr. David T. Osborne; Exxon Oil Company, Houston, Tex.

Dr. Chuin T. Yeh; National Tsin-Hua University, Taiwan

Dr. David G. Keil; University of Washington, Seattle, Wash.

Dr. Gregory N. Suess; Center for Naval Analysis, Arlington, Va.

Dr. Jorge J. Ahumada; UIS, Bucharamanga, Columbia

Dr. Thomas C. Schwab; Engelhard Industries, Plainfield, N.J.

Mr. Scott D. Gleditsch; Hannemann Medical School, Philadelphia, Pa.

It is a pleasure to report that a ninth student, Mr. Joseph A. Cowfer, nearly has completed his thesis and will be submitting it within the next one to two months. He has accepted a position at B. F. Goodrich in Cleveland, Ohio.

TABLE OF CONTENTS

PART I. GENERAL REPORT, by J. V. Michael	1
A. Introduction	1
B. Personnel	3
C. Facilities	3
D. Manuscripts submitted for publication	4
E. Manuscripts accepted for publication	4
F. Publications	4
G. Manuscripts in Preparation	5
H. Theses	6
I. Acknowledgements	7
 PART II. RESEARCH PROGRESS	
A. Experiment A - Discharge Flow-Lyman α Detection, by J. V. Michael	8
B. Experiment B - Time Resolved Detection of Hydrogen Atoms, by K. P. Lynch	9
C. Experiment C - Steady-State Hydrogen Atom Analysis with Lyman α Absorption Photometry.....	34
D. Experiment D - Shock Tube, by T. C. Schwab	35
E. Experiment E - Coupled Flow Reactor-T.O.F. Mass Spectro- meter, by J. A. Cowfer and K. P. Lynch.....	57
F. Experiment F - Absolute Quenching Cross Sections of (Hg^3P_1) with Various Molecules, by S. D. Gleditsch ...	101
G. Experiment G - Theoretical Calculations, by J. A. Cowfer and K. P. Lynch	112

In past years the contract has supported the construction of and work with six experimental apparatuses. All apparatuses are or have been operable and have been used to measure rate constants for elementary gas phase reactions. The major effort has been on room temperature reactions of hydrogen atoms with substrate molecules, however, certain high temperature reactions have been studied also. In addition to experimental studies, an important aspect of the work of this contract has been continuing theoretical interpretation of the experimental results.

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 either have been or are operational and have yielded data of interest to radiation chemists, photochemists, and chemical kinetics. Each project with particular emphasis on the past year's progress will be discussed in Part II of this report.

B. PERSONNEL

The principal investigator on this project is Associate Professor J. V. Michael of Carnegie-Mellon University. The Contract has supported thesis research of four graduate students. These are:

Mr. Thomas C. Schwab; B.S., University of Pittsburgh, 1968.

Mr. Joseph A. Cowfer; B.S., Duquesne University, 1969.

Mr. Kevin P. Lynch; B.S., Mt. St. Mary's College, 1968
M.S., University of Wisconsin, 1970.

Mr. Scott D. Gleditsch; B.A., Thiel College, 1971.

Two of these students are now terminated. Mr. Gleditsch has submitted an M.S. thesis, and Mr. Cowfer has nearly completed his Ph.D. thesis. He is currently serving three months active duty as a First Lieutenant in the U.S. Air Force in fulfillment of his ROTC obligation.

C. FACILITIES

The laboratories which house this project are contained in the Mellon Institute building at Carnegie-Mellon University. The personnel working under this project have access to a large variety of helpful resources and resource personnel which are invaluable for successful research. These include 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 enjoys 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 are also available to the project on a per job basis.

D. MANUSCRIPTS SUBMITTED FOR PUBLICATION

J. R. Barker and J. V. Michael, "Steric Collision Models for Reaction Cross Sections," submitted to J. Chem. Phys.

J. A. Cowfer and J. V. Michael, "Experimental Investigation of Nonequilibrium Kinetic Isotope Effects in Chemically Activated Ethyl Radicals," submitted to J. Chem. Phys.

J. A. Cowfer and J. V. Michael, "Theoretical Investigation of Nonequilibrium Kinetic Isotope Effects in Chemically Activated Ethyl Radicals," submitted to J. Chem. Phys.

E. MANUSCRIPTS ACCEPTED FOR PUBLICATION

R. L. Klobuchar, J. J. Ahumada, J. V. Michael, and P. J. Karol, "Details of Dead Time Losses in Scaling and Multiscaling," Review of Scientific Instruments.

R. L. Klobuchar, J. J. Ahumada, J. V. Michael, and P. J. Karol, "An Accurate Method of Photomultiplier Gain Determination," Review of Scientific Instruments.

F. PUBLICATIONS

An Experimental Estimate of the Oscillator Strength of the $^2P_{3/2,1/2} \leftarrow ^2S_{1/2}$ 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).

Reaction of $H + C_2H_4$: Comparison of Three Experimental Techniques, J. R. Barker, D. G. Keil, J. V. Michael, and D. T. Osborne, J. Chem. Phys. 52, 2079 (1970).

Absolute Cross Section for $\text{Hg}(^3\text{P}_1) + \text{H}_2$ and the Imprisonment Lifetimes for $\text{Hg}(^3\text{P}_1)$ 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 $\text{H} + \text{O}_2$, $\text{H} + \text{NO}$, and $\text{H} + \text{CO}$, J. J. Ahumada, J. V. Michael, and D. T. Osborne, J. Chem. Phys. 57, 3736 (1972).

Reaction $\text{H} + \text{C}_2\text{H}_4$: 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).

Chemical Kinetic Effects of Walls on Active Species, J. J. Ahumada and J. V. Michael, J. Phys. Chem. 78, 465 (1974).

Absolute Quenching Cross Sections of $\text{Hg}(^3\text{P}_1)$ with Various Molecules, J. V. Michael and G. N. Suess, J. Phys. Chem. 78, 482 (1974).

G. MANUSCRIPTS IN PREPARATION

The Reactions of H and D with Silane and Methyl-silanes, J. A. Cowfer, K. P. Lynch, and J. V. Michael.

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

The $\text{H} + \text{C}_2\text{H}_2$ Reaction with Deuterated Variations, J. A. Cowfer, D. G. Keil, and J. V. Michael.

An RRKM Theoretical Interpretation of the $\text{H} + \text{C}_2\text{H}_2$ Reaction and Deuterated Variations, K. P. Lynch and J. V. Michael

Further Results for H Atom Wall Reactions in Seven Heat Bath Gases,

K. P. Lynch and J. V. Michael.

The H + H + M Reaction at Room Temperature in H₂, He, Ne, Ar, Kr, and N₂,

K. P. Lynch, J. V. Michael, and T.C. Schwab.

A Test of Mirel's Non-ideal Shock Tube Theory, J. V. Michael and T. C. Schwab.

The Dissociation of H₂ in a Shock Tube, J. V. Michael and T. C. Schwab.

Further Hg(³P₁) Quenching Studies, S. D. Gleditsch and J. V. Michael.

H. THESES (Ph.D.)

I. Experimental Determination of the Oscillator Strength of the ²P_{3,1/2} ← ²S_{1/2} Transition of Atomic Hydrogen. II. Absolute Rate Constants for the Reactions H + C₂H₄ and H + C₂D₄; 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 + C₂H₄, H + C₂D₄, D + C₂D₄, H + C₂H₂, H + O₂, 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 + C₂H₄. II. Absolute Quenching Cross Sections of Hg(³P₁) with Various Molecules. III. A Study of Charge Contraction in Bonded Hydrogen Atoms from X-Ray Diffraction Data, by Gregory Neil Sues.

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

THESIS (M.S.)

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

I. ACKNOWLEDGEMENTS

The principal investigator and graduate students whose research as been supported completely by the Atomic Energy Commission under Contract AT(11-1)-3242 wish to gratefully acknowledge this support. We also acknowledge the cooperation and support of Professor Albert A. Caretto, Jr., former Chairman of the Department of Chemistry of Carnegie-Mellon University, and the computer services of the NMR facility (NIH Grant RR00292) under the direction of Professor A. A. Bothner-By.

A. Experiment A

Discharge Flow-Lyman α Detection

This experiment combines the well known technique of discharge flow with Lyman α absorption spectrometry for analysis of H atom concentrations. This was the original experiment which was proposed under the contract. Even though this apparatus was not operable during the past year, results have been obtained in previous years with it.¹⁻³ The results obtained have been of prime importance in all of the Lyman α absorption work done in these laboratories. As pointed out in the 1972-73 Annual Progress Report (COO-3242-7),⁴ the calibration of John Barker has served as the principal source for absolute H atom inferences.

During the past year, the theme of this project has been used, however, since new line absorption calculations have been carried out in order to specify growth curves for Experiments B and D (up to 3000°K).⁵ These calculations are consistent with the earlier calibrations^{1,4} and with the two level model for resonance lamps which was proposed by Braun, Bass, and Davis.⁶ Thus, absolute H can be specified within $\pm 20\%$ confidence limits for both apparatuses. We have used this information to determine the termolecular rate constants for $H + H + M$ (Experiment B), and the H_2 dissociation rate constant for $H_2 + Ar$ (Experiment D).

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Experiment B

Time Resolved Detection of Hydrogen Atoms

Introduction

Previous work^{1,2} in this laboratory has demonstrated that the time dependence of hydrogen atom concentrations in a cylindrical Lyman α photometric system¹ can be successfully predicted from a general theory of the chemical kinetics effects of walls on active species. The theory considers the coupling between homogeneous first order reactions, diffusion, and heterogeneous reaction at the walls of an active species in a cylindrical system. The results for hydrogen atoms in the presence of third body species: molecular hydrogen, and krypton have been very satisfying and have stimulated attempts to further test the theory with a variety of third body gases. Also prompting further investigation were the difficulties encountered in predicting the decay of atoms at high pressures that required an unexpected variation in the single parameter of the model calculations: ϵ , the wall recombination coefficient. However, in order to obtain maximum information from further work it was decided that the system should be modified to allow experiments to be performed in the previously inaccessible region of 1 to 2 atmospheres pressure of third body gas.

In addition to the information that could be obtained to further our understanding of the applicability of the theory to this system, it was apparent that further work on the theoretical calculations of the $H + C_2H_2/He$ system required experimental values for the high pressure limiting rate constant for that reaction.³ Previous work had indicated that pressures in

excess of an atmosphere would be required for this measurement.¹

Further motivation for this project was the possibility of measuring the rate constants for the reaction

where M represents a variety of possible third body gases. This experiment however requires an accurate knowledge of the absolute hydrogen atom concentration, rather than an accurate knowledge of relative atom concentrations necessary for the other two experiments. The details of the line absorption calculation that was performed to obtain this information and preliminary results of our experiments after modifying the apparatus are presented below. The apparatus has been described previously.¹

I. Effects of Walls on H Atoms: Room Temperature Results in Seven Heat Bath Gases

Data is now available to test the theory of wall effects on hydrogen atoms for seven third body gases: H_2 , He, Ne, Ar, Kr, Xe, N_2 . For all of the systems except Xe, the data ranges from pressures of 100 torr to 1400 torr. The Xe system is limited to the pressure range 10 to 200 torr since pressures of Xe in excess of 200 torr absorb Lyman α radiation.

Comparisons of theory and experiment are made in Figures 1 through 7; the experimentally determined values of k_1 , the first order rate constant for decay of H atoms due to wall recombination are plotted versus the pressure of the third body gas. The smooth curves are the theoretically predicted values of this rate constant $D\alpha_1^2$. The Lennard-Jones potential parameters for H atoms are available^{4,5} and can be combined with the known parameters for the other gases; values for the binary diffusion coefficients of H atoms

in various gases were calculated from the expression⁶

$$D_{1,2} = \frac{2.6280 \times 10^{-3} T^{3/2} ((M_1 + M_2)/2M_1M_2)^{1/2}}{P \sigma_{12}^2 \Omega_{12}^{(1,1)*} (T_{12}^*)} \quad (\text{II})$$

and are listed in Table 1. For all of the theoretical calculations, the zero pressure wall termination rate constant, $\frac{\bar{c}\epsilon}{2a}$, was assumed to have a value of 25 sec^{-1} which implies $\epsilon = 3.37 \times 10^{-4}$.

All of the systems studied with the exception of H + wall in Ne showed good agreement between predicted and observed rate constants at pressures less than 400 torr. A common feature of all of these systems is the requirement that ϵ vary at high pressures to obtain satisfactory agreement with the observed values of k_1' . Variation of ϵ can be justified² but the observation that it must be variable in all systems at high pressure prompted further investigations of the model assumptions.

Extensive modifications of the theoretical boundary conditions were attempted in an effort to duplicate the experimental behavior: none of these resulted in any change in the predicted rate constants at high pressure. If it is assumed that ϵ remains constant, the theory predicts that decay constants obtained from $\ln[H]$ vs. time plots will be $D\alpha_1^2$ in the absence of reactant and $D\alpha_1^2 + k$ in the presence of reactant. Thus, the high pressure behavior of the observed rate constant could be attributed to a variation in k for some common reactant in all of the systems observed. The experimental observation that the rate constants either decrease only slightly with increasing pressure or approach a constant value would imply that either $k = 4.8 \text{ sec}^{-1}$ independent of pressure or that k increase slightly with pressure. Then the theoretical quantity

$D\alpha_1^2 + k$ would simulate the observed high pressure behavior.

This entire presentation, however, presumes the presence of a common reactant in 7 samples of research grade gases that are very carefully handled to avoid contamination. We do not believe that these samples are contaminated with any such impurity. However, the technique of production of hydrogen atoms in this system is the $\text{Hg}(^3\text{P}_1)$ sensitization of molecular hydrogen; and a relatively constant amount of mercury was present in all of the systems studied. A series of experiments is now being undertaken to determine the effect of varying Hg concentration on the observed rate constants at high pressures. In particular the reactions

are of interest. Reaction (I-2) is known to occur rapidly;⁷ variation of mercury concentration should provide a probe for the postulated rate controlling process, reaction (I-1), and give a value for the $\text{H} + \text{Hg}(^1\text{S}_0) + \text{M}$ rate constant in seven third bodies.

II. Hydrogen Atom Recombination Rates

The Lyman α detection system used in these experiments has been described previously in connection with high temperature shock tube experiments.¹ The source of Lyman α radiation is a counterflow He discharge lamp of the type originally described by Davis and Braun.⁸ The ability to characterize the lamp output and absorption behavior of such systems has been demonstrated in an elegant calibration experiment.¹

A line absorption calculation was made for the present system with only slight changes in the parameters used in the previous calibration. These

modifications were necessitated by small changes in the geometries of the lamps which were used in the two systems. The calculated absorption curve is presented in Figure 8 as percent transmission vs. Nl (concentration in atoms cc^{-1} , N , times cell path length in cm, l). The need for absolute atom concentrations in this experiment is apparent from the discussion that follows.

The important reactions in these experiments are

where reaction (II-1) also includes any first order H atom termination of the type postulated in part I. The rate of H atom depletion is

$$-\frac{d\text{H}}{dt} = 2k'_r[\text{H}]^2[\text{M}] + k_w[\text{H}] \quad (\text{II-3})$$

or

$$-\frac{d\text{H}}{dt} = k_r[\text{H}]^2 + k_w[\text{H}] \quad (\text{II-4})$$

where

$$k_r = 2k'_r[\text{M}].$$

Upon integration equation (II-4) yields the expression,

$$e^{-k_w t} = \frac{[\text{H}]}{[\text{H}]_0} \left(\frac{k_r[\text{H}]_0 + k_w}{k_r[\text{H}] + k_w} \right),$$

where $[\text{H}]_0$ is the initial concentration of H atoms, and $[\text{H}]$ is the atom concentration of time t . Thus, a knowledge of the absolute atom concentration provides a method for calculating k_r from the expression

$$k_r = \frac{k_w \left(\frac{[H]_0}{[H]} e^{-k_w t} - 1 \right)}{[H]_0 (1 - e^{-k_w t})} \quad (II-5)$$

The quantity k_w is obtained from plots of $\ln[H]$ vs. t after sufficient time has elapsed for reaction (II-2) to become unimportant.

The record of a typical experiment is presented in Figure 9; the data obtained from this photograph is presented in Figure 10. The value of k_w was obtained from the data between $t = 200$ to $t = 550$ msec; then values of k_r were tabulated for each experimental point from $t = 20$ to $t = 320$ msec, and these were averaged to determine the experimental k_r for that particular experiment. This experiment was repeated at a number of different pressures of M, the third body gas, and the final value of k_r was obtained from a plot of k_r vs. pressure. The experimental values listed in Table 2 and shown in Figures 1 - 16 are reported here as preliminary results; further experiments are required, but the reported values are probably within $\pm 30\%$ of the final results.

The desirability of obtaining experimental determinations of these rate constants for work of current theoretical interest is expressed in reference 9. Three of the preliminary results reported here are supported by previous reports,⁹ and this study reports values for three third body gases that have not been reported previously.

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Table I

M	Lennard-Jones Parameters ^(a)		Calculated Binary Diffusion Coefficients ^(c)
	$\sigma(\text{\AA})$	$\epsilon/k(^{\circ}\text{K})$	$D_{H,M}$
H	1.67 ^(b)	217 ^(b)	---
H ₂	2.97	33.3	1835/P
He	2.576	10.22	2264/P
Ne	2.789	35.7	1646/P
Ar	3.465	116	1028/P
Kr	3.61	190	875/P
Xe	4.055	229	714/P
N ₂	3.681	91.5	991/P

(a) unless noted all values from reference 6

(b) reference 4

(c) P = pressure in torr

Table 2

THIRD BODY SPECIES	ROOM TEMPERATURE H ATOM RECOMBINATION RATE CONSTANTS ^a (k_r) ($\text{cm}^6 \text{ molecules}^{-2} \text{ sec}^{-2}$)
H_2	8.97×10^{-33} ; $8.1 \pm 0.4 \times 10^{-33}^b$
He	11.7×10^{-33} ; $7.0 \pm 0.4 \times 10^{-33}^b$
Ne	14.9×10^{-33}
Ar	9.49×10^{-33} ; $9.2 \pm 0.6 \times 10^{-33}^b$
Kr	21.2×10^{-33}
N_2	10.3×10^{-33}

(a) all values from this work unless noted

(b) values from reference 9.

H_2

N

h₁

Kr

Fig. 5

Xe

1-13.6

23

N_2

Fig. 7

Fig. 8

25

%T

K&E SEMI-LOGARITHMIC 46 5133
2 CYCLES X 140 DIVISIONS
MADE IN U. S. A.
KEUFFEL & ESSER CO.

$N \times 10^{-12}$

Fig. 9

Fig. 10

K&E SEMI-LOGARITHMIC 46 5493
3 CYCLES X 70 DIVISIONS
MADE IN U.S.A.
KEUPPEL & ESSER CO.

$[H] \times 10^{-12} (\text{atoms cc}^{-1})$

100 200 300 400 500 600 700
time (msec)

Fig. 11

46 1513

K&E 10 X 10 TO THE CENTIMETER 18 X 25 CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.

$k_r \times 10^{13}$

H_2 Pressure (torr)

Fig. 1.2

46 1513

K₀Σ 10 X 10 TO THE CENTIMETER 18 X 25 CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.

$k_r \times 10^{13}$

Fig. 13

30

46 1513

K-E 10 X 10 TO THE CENTIMETER 18 X 25 CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.

$k_r \times 10^{13}$

Fig. 14

31

46 1513

10 X 10 TO THE CENTIMETER
KEUFFEL & ESSER CO. MADE IN U.S.A.

K.E.

$K_r \times 10^{13}$

Ar Pressure (torr)

Fig 15

32

46 1513

K.E. 10 X 10 TO THE CENTIMETER 18 X 25 CM.
KEUFFEL & ESSER CO. MADE IN U.S.A.

$k_r \times 10^{13}$

Kr Pressure (torr)

Fig. 16

46 1513

10 X 10 TO THE CENTIMETER

KEUFFEL & ESSER CO. MADE IN U.S.A.

K.E.

$k_r \times 10^{13}$

N₂ Pressure (torr).

C. Experiment C

Steady-State Hydrogen Atom Analysis with Lyman α Absorption Photometry

This experiment combines Lyman α absorption photometry with the steady-state mercury photosensitization of molecular H_2 . It has been used in the past to measure the cross section of the $Hg(^3P_1) + H_2$ reaction.¹ Also an experiment was designed in which rate constants for H with substrates relative to the $H + C_2H_2$ could be measured.² Additional experiments on the mechanism of the mercury photosensitized decomposition of hydrogen have been obtained and will be published along with similar results from experiment B.³

This experiment has been discontinued and the apparatus has instead been used for $Hg(^3P_1)$ quenching studies.

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D. Experiment D

This experiment combines Lyman α absorption spectrometry with a shock tube in order to observe the high temperature reactions of hydrogen atoms. Results are now complete on two projects with this equipment: (a) The test of Mirel's non ideal shock tube theory, and (b) the dissociation of molecular hydrogen. This work has served as the basis of a Ph.D. thesis by T. C. Schwab. The equipment and some preliminary results have been described in previous Annual Progress Reports. In the paragraphs to follow are particularly pertinent sections of Dr. Schwab's thesis. For a complete understanding of the work associated with this equipment, the reader is referred to the aforementioned thesis. It should also be noted that the conclusions which are presented on the dissociation of hydrogen are tentative and further work is progressing in order to rationalize these data.

E. The Effect of Boundary Layer Development on Kinetic Investigations.

The formation of a boundary layer in the shock processed gas contributes to the "non-ideal" behavior of shock tube flow. In order to describe the effect of this behavior on kinetic investigations (see Appendix I) it is necessary to determine the hydrodynamic character (laminar or turbulent flow) of the boundary layer gas. It has been shown^{8,30,43} that a measure of the temperature profile of the boundary layer gas adjacent to the wall defines its hydrodynamic state. That is, a constant temperature profile (constant rate of heat transfer to the wall) implies a laminar flow and a temperature profile that increases with time (an increasing rate of heat transfer to the wall) signifies a turbulent flow. It was possible to measure this temperature profile with the use of a modified shock velocity gauge.

The heat transfer gauge in the velocity detection mode only responds to the initial voltage increase which signals the arrival of the shock front. This design does not permit a time-dependent observation of the shock processed gas. In order to obtain a temporal record of the boundary layer gas, the continuous voltage output from the gauge must be monitored, and then, this voltage record is correlated with the temperature of the boundary layer gas. This voltage-temperature

relationship was previously described in the discussion of shock velocity gauge design. The details of this experiment are as follows.

The velocity gauge immediately before the observation station was chosen for this experiment. This permits a hydrodynamic analysis of boundary layer gas at the time of the kinetic observation. The voltage output of the gauge was monitored oscilloscopically (Tektronix model 549 storage oscilloscope with a type 1A1 preamplifier) at a point just after the first stage of amplification. All other stages of the gauge electronics were disconnected to avoid electronic noise. The sweep of the oscilloscope was externally triggered with the output of the velocity gauge which is two gauges before the observation station. An oscilloscope camera was used to record the voltage profile of the heat transfer gauge. Three Polaroid photographs of this display are presented in Figure 8. The first photograph represents a completely laminar boundary layer flow. The second photograph describes a situation in which the boundary layer flow is first laminar and then becomes turbulent at the point of transition. The third photograph shows a completely turbulent flow. The arrival time of the driver gas (contact surface) was determined from the Lyman- α experimental records. This method was previously described in the Lyman- α photometry section.

The interpretation of the kinetic experiments is simplified if the boundary layer gas flow is defined by either a completely laminar or completely turbulent flow. Therefore, several experiments were carried out to determine the experimental conditions under which these hydrodynamic situations are described. The results are as follows.

SHOCK FRONT CONTACT SURFACE

③

②

①

SHOCK FRONT CONTACT SURFACE

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TRANSITION

It is a well-known⁴⁵ fact that the origin of turbulence (transition point) in a laminar flow shows a very weak dependence on mach number. The significant parameters which determine the hydrodynamic character of the boundary layer are shock tube diameter and the initial experimental gas pressure. Of course, in this set of experiments, the shock tube diameter is a constant equal to 4.06 cm. Therefore, the variable in this set of experiments was the initial experimental gas pressure. The results of these experiments are shown in Table 1. Experimental gas pressures, P_1 , were varied from 2.5 to 24.8 torr. The percentage of laminar and/or turbulent flow was calculated from the ratio of the observed time for laminar and/or turbulent flow, divided by the total observation time for the shocked gas. As previously stated, the total observation time was determined from the Lyman- α experimental records. The results in Table 1 show that pure laminar flow was observed at an experimental pressure of 3.5 torr or less and pure turbulent flow was observed at a pressure of 8.5 torr or greater. A mixture of laminar and turbulent flow is obtained in the intermediate pressure range (3.5-8.5 torr). It is obvious from these experiments that the conditions under which pure turbulent flow exists offer a wide range of experimental conditions for kinetic investigations. Thus, the decision was made to perform all kinetic studies under those conditions which give pure turbulent boundary layer flow.

The ability to predict the effects of boundary layer flow on kinetic studies depends on the determination of the time or distance between the shock front and contact surface (see Appendix I for a complete discussion). Since it is not always possible to make this

Table 1
The Boundary Layer Hydrodynamic Character for
Experiments with Different Initial Pressures

M_s	P_1 (torr)	Hydrodynamic Character	
		Percent Laminar	Percent Turbulent
4.44	2.5	100	0
4.76	3.5	100	0
5.16	4.8	73	27
5.88	5.0	64	36
5.67	5.3	72	28
5.32	6.8	26	74
5.49	8.5	0	100
4.88	8.9	0	100
5.02	8.9	0	100
4.96	9.0	0	100
5.54	9.0	0	100
4.32	10.7	0	100
5.35	11.0	0	100
4.42	17.0	0	100
4.54	22.0	0	100
4.53	23.0	0	100
4.18	23.5	0	100
4.47	24.8	0	100

measurement in a shock tube, it would be useful to have a theory to predict this separation time or distance. Mirels^{46,47} has proposed such a theory. An analysis of this theory is presented in Appendix I. As was previously described, the measurement of the separation time can be made with this apparatus. Therefore, a set of experiments were carried out to check Mirels' theoretical predictions.

The experiments were designed to investigate the separation time with turbulent boundary layer flow. The results of these experiments and a comparison with Mirels' predictions are presented in Table 2. Experimental pressures were varied from 8.9 to 34.14 torr. Contact surface arrival time was measured by the procedure discussed in the Lyman- α photometry section. The results are also presented in a ratio form ℓ/ℓ_m , where ℓ is the measured separation distance (calculated from the product of observation time and shock velocity) and ℓ_m is the quasi-steady case of maximum separation described by Mirels.^{46,47} The reader is referred to Appendix I, Section D for a complete discussion of ℓ_m with appropriate theory, equations, and graphs. A comparison of the experimental ℓ/ℓ_m ratio and theoretical ℓ/ℓ_m ratio shows that Mirels' theory underestimates the separation distance by 15% on the average. The comparison is quite good with this apparatus. Belles and Brabbs⁴⁸ have carried out a similar experiment and have seen this same effect. They report that Mirels' theory underestimates the separation distance by as much as 60% in their apparatus. It appears that the applicability of Mirels' predictions is dependent on the particular apparatus and therefore when possible, a test of Mirels' theory should be made.

The measured value of separation distance, ℓ , is used to interpret the experimental results presented in this work.

Table 2
A Comparison of the Experimentally Determined and Theoretically Calculated
Separation Distances for a Range of Experimental Pressures

M_s	P_1 (torr)	Contact Surface Time (μ sec.)		ℓ (Theor.)	ℓ (Exp.)	$\frac{\ell(\text{Exp.})}{\ell(\text{Theor.})}$ ^a
		(Experimental)	(Theoretical)	ℓ_m	ℓ_m	$\ell(\text{Theor.})/\ell_m$
4.88	8.90	220.1	196.2	.845	.950	1.12
5.02	8.90	215.0	189.9	.850	.962	1.13
4.96	9.00	205.2	197.1	.842	.876	1.04
4.32	10.70	300.1	240.5	.820	1.031	1.26
4.45	18.84	251.4	285.4	.781	.884	1.13
4.53	19.13	245.5	280.3	.783	.840	1.14
4.57	19.33	243.4	295.0	.780	.945	1.21
4.52	19.55	245.4	310.0	.772	.973	1.26
4.18	23.50	310.0	286.0	.760	.824	1.08
4.17	31.17	295.1	330.2	.731	.816	1.12
4.24	31.51	289.1	337.0	.730	.851	1.16
4.17	32.37	294.7	334.0	.722	.817	1.13
4.35	34.14	279.6	340.1	.720	.876	1.22

^a The average deviation from unity is + 0.15.

IV. DISCUSSION

To the knowledge of this investigator, no accurate determination of order for the dissociation of hydrogen in argon has been previously determined. Earlier studies²⁰⁻²⁶ of this reaction have been carried out with the assumption that the order dependence for both hydrogen and argon is 1.0. This assumption is contrary to the results of the order determination in this work. As previously stated, the order for H_2 was found to be 0.55 and the order for argon was 1.0.

The comparison of the results in this work and the most recent studies by Myerson and Watt²⁶ are presented in Figure 11. The absolute rate constant, k_d , has been determined with the assumption that the order dependence in hydrogen and argon is 1.0. The agreement in this comparison is reasonably good. This agreement implies the proper use of the experimental technique and the validity of the data reduction method. The sensitivity of this present work is much better than that of Myerson and Watt²⁶ and Breshears and Bird.²⁵

The resonance source of Lyman- α used by Myerson and Watt²⁶ was similar to that used in this work. However, a mixture of 10% hydrogen in helium was used. As stated in the Experimental Discussion, even a small amount of hydrogen increased the photon flux and improved the signal-to-noise ratio, but the sensitivity for hydrogen atom detection was seriously impaired. This effect of hydrogen addition to the resonance source has also been observed by Braun.⁴⁹ Therefore, it must be assumed that Myerson and Watt²⁶ sacrificed sensitivity for a large intensity of very highly reversed Lyman- α radiation.

Figure 11

An Arrhenius plot ($\ln k_d$ vs. $1/T^\circ K$) for the experiments listed in Tables 3 and 4 with the assumption of order, 1.0 for Ar and 1.0 for H_2 . The solid line is the work of Breshears and Bird²⁵ and the dashed line is the work of Myerson and Watt.²⁶ The units for k_d are $\text{cc mole}^{-1} \text{sec}^{-1}$.

Breshears and Bird²⁵ used a laser schlieren technique to monitor the density profile behind the shock. The mixtures of hydrogen and argon which were studied ranged from a maximum of 20% hydrogen to a minimum of 5% hydrogen. Under these conditions, the efficiency of the rare-gas collision partner cannot be independently determined, that is, the observed rate constant $k_{d(\text{obs})}$ is assumed to be a linear function of composition,

$$k_{d(\text{obs})} = \sum_M x_M k_d^M, \quad (10)$$

where k_d^M is the rate coefficient due to the H_2 -M (M is H_2 or Ar) collisions and x_M is the mole fraction of species M in the mixture. Equation (10) is then used to extract the contribution of the various M to the overall rate. The experimental observations of induction periods for diatomic dissociations^{50,51} clearly indicate that the assumptions implicit in Equation (10) are not valid during the early course of the reaction. Thus, the sensitivity of this technique is limited for experimental reasons, i.e., the high minimum concentrations of 5% hydrogen which was used; and for theoretical reasons, i.e., Equation (10) is not valid in the early stages of the reaction.

The results of the order experiments in this work could possibly suggest the presence of an oxygen impurity in the gas mixture.

The reason that oxygen impurity might be suspected is that the effect of added oxygen is to increase the rate of H-atom production.²⁶ This effect would tend to spread the parallel lines in the order determination (Figures 9 and 10) and, therefore, predict a lower order than

would be expected. This catalytic effect of oxygen can be explained in terms of the competition for hydrogen-atom production between the reaction

and the reactions important at these low atom concentrations,

It has been shown²⁶ experimentally that reaction (14) is rate determining. Reaction (12) can be eliminated as a serious contributor to the mechanism for hydrogen-atom production because both too slow a rate and an incompatible temperature dependence. Also, reaction (13) is not rate determining for the conditions of low concentration in the shock tube studies. Myerson and Watt²⁶ determined that the catalytic effect of oxygen in their hydrogen dissociation experiments was accurately predicted by this mechanism (reactions 11-15) where reaction (14) is the rate determining step.

In this work, the presence of an oxygen impurity is refuted for two particular reasons. The purity and handling of the gases has been described in Section F of the Experimental Discussion. The total

impurity level of O_2 in the gas mixtures was less than 2 ppm. The leak rate of the experimental section is so low that less than 5 ppm of air could be in the mixture. Also, a number of experiments were carried out with small amounts (100-1000 ppm) of oxygen added to the mixture. The results of these experiments showed a definite delay (up to a few hundred microseconds particle time at temperatures of 2000°K or less) in the production of hydrogen atoms. This well-known induction time effect was not observed to the same extent in pure H_2 -Ar mixtures at the same experimental conditions.

It is assumed, from all the previous considerations, that the order determination, 1.0 for argon and 0.55 for hydrogen, is correct. An Arrhenius plot ($\ln k_d$ vs. $1/T^\circ K$) of the absolute rate constants, k_d , which are calculated with the experimentally determined orders, is presented in Figure 12. A least squares fit of the experimental data gives an expression for the rate constant in the form,

$$k_d = 10^{5.81 \pm .23} \exp \left(\frac{-45,200 \pm 2,300}{RT} \right) \text{cc}^{0.55} \text{mole}^{-0.55} \text{sec}^{-1} \quad (16)$$

A comparison of this result and the expression for k_d calculated with the assumption of 1.0 order dependence for both hydrogen and argon shows a remarkable effect. The statistics of the experimental data presented with the experimentally determined order (Equation 16) are significantly better than the statistics of experimental data presented with the assumption of 1.0 order for both hydrogen and argon (Equation 7). Specifically, the standard deviation in the activation energy was improved from $\pm 21.2\%$ in k_d (Equation 7, order 1.0 for both H_2 and Ar) to $\pm 5.1\%$

Figure 12

An Arrhenius plot ($\ln k_d$ vs. $1/T^\circ\text{K}$) for the experiments listed in Tables

for k_d (Equation 16, order 0.55 for H_2 and 1.0 for Ar). The standard deviation in the preexponential factor decreased from $\pm 11.7\%$ (Equation 7) to $\pm 4.0\%$ (Equation 16).

The comparison of statistics in the two methods (Equation 7 and 16) of absolute rate constant determination is strong evidence that the correct order dependence for hydrogen is 0.55 and the order dependence with respect to argon is 1.0. However, the activation energy, 45.2 kcal predicted by this order determination is low for the simple mechanism (Equation 1) of hydrogen dissociation. It is of interest to note that in the investigation by Bauer and Ossa⁵² of the isotope exchange rates of H_2 and D_2 , an activation energy of 42.6 kcal was predicted. The order dependence of the exchange reaction was found to be 0.98 for Ar, 0.66 for D_2 , and 0.38 for H_2 . The results from the present study could possibly indicate that the mechanism for H_2 - D_2 exchange is atomic and not the four-center mechanism that was proposed.⁵²

The recent work of Kern and Nika⁵³ on the H_2 - D_2 reaction predicts an activation energy of 44.4 kcal. They observed a quadratic time dependence in the product HD and suggested an atomic mechanism for the exchange reaction. It is as follows:

This mechanism provides an explanation for the quadratic time dependence but requires an activation energy on the order of 110 kcal.

It is quite difficult to suggest a mechanism for hydrogen dissociation in argon with an order dependence of 0.55 for hydrogen. One possible mechanism, which predicts an activation energy closer to the bond dissociation energy, 103.3 kcal, will now be presented.

The reactions in the mechanism are:

where reaction (17) corresponds to the vibrational relaxation of hydrogen. The rate of production of $\text{H}_{2\nu}$ is presented as,

$$\frac{d[\text{H}_{2\nu}]}{dt} = k_{17}[\text{H}_2][\text{M}] - (k_{-17} + k_{18}) \text{M} [\text{H}_{2\nu}] \quad (19)$$

and integration of Equation (19) gives the result,

$$[\text{H}_{2\nu}] = \frac{k_{17}[\text{H}_2]}{(k_{-17} + k_{18})} \left[1 - e^{-(k_{-17} + k_{18}) [\text{M}] t} \right] \quad (20)$$

The rate of formation of H-atoms is expressed as

$$\frac{d[\text{H}]}{dt} = 2k_{18}[\text{M}][\text{H}_{2\nu}] \quad (21)$$

and substitution of Equation (19) gives the result,

$$\frac{d[H]}{dt} = \frac{2k_{17}k_{18}[M][H_2]}{(k_{-17} + k_{18})} \left[1 - e^{-(k_{-17} + k_{18})[M]t} \right] \quad (22)$$

The exponential in Equation (22) can be presented as a series expansion in the form,

$$e^x = 1 + x + \frac{x^2}{2!} + \text{etc.} \quad (23)$$

where $x = -(k_{-17} + k_{18})[M]t$.

If all terms but the first term in the series are considered to be negligible, Equation (22) can be rewritten in the form

$$\frac{d[H]}{dt} = 2k_{17}k_{18}[H_2][M]^2t \quad (24)$$

This expression shows the same relative order dependence that was experimentally determined. Integration of Equation (24),

$$[H] = k_{17}k_{18}[H_2][M]^2t^2, \quad (25)$$

indicates a time-squared dependence in hydrogen atom concentration.

In order to check the validity of this mechanism, the experimentally determined $[H]$ were plotted as a function of time squared for all the experiments. The results from these graphs all showed the same effect. This was an initial linear slope for early (a few hundred microseconds) particle heating times after which a negative deviation

occurred in the slope. This result would appear to indicate that the mechanism is not valid in the later part of the reaction. Therefore, the absolute rate constant $k_d = k_{17}k_{18}$ was determined from the initial slopes of the $[H]$ vs. t^2 plots and Equation (25). The results of the k_d determination are presented in Figure 13. A least squares fit of the experimental data gives an expression for k_d in the form

$$k_d = k_{17}k_{18} = 10^{(22.2 \pm .4)} \exp\left(\frac{-78,800 \pm 4,100}{RT}\right) \quad (26)$$

The statistics of this result, a standard deviation of $\pm 5.2\%$ in the activation energy and $\pm 1.8\%$ in the preexponential factor, are quite good. Also, the activation energy of 78.8 kcal is a reasonable value for the dissociation reaction.

It would appear, from this study, that the reaction mechanism presented in Equations (17) and (18) is a possible representation of the early part of the dissociation reaction. The linear dependence of $[H]$ on time, after the early part of the dissociation suggests that perhaps two mechanisms are necessary to describe the dissociation reaction. The first mechanism would be that which is described in Equations (17) and (18) and the second would be the simple mechanism described in Equation (1).

It is hoped that this study of order determination will instigate a theoretical investigation of the mechanism for hydrogen dissociation.

Figure 13

An Arrhenius plot ($\ln k_d$ vs. $1/T^\circ\text{K}$) for the experiments listed in Tables 3 and 4 with the assumption of order, 1.0 for H_2 and 2.0 for Ar. The units of k_d are $\text{cc}^2 \text{mole}^{-2} \text{sec}^{-1}$.

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Experiment E

Coupled Flow Reactor-T. O. F. Mass Spectrometer

Introduction

During the past year this equipment has been operative and has been used on two projects. New and more accurate rate constants for the reaction $H + C_2D_4$ have been obtained. In addition the rate constants for $D + C_2H_4$ and $D + C_2D_4$ have been measured at room temperature as a function of pressure. These measurements have been interpreted in terms of a self-consistent RRKM theoretical framework which is consistent with earlier work. This theoretical work is reviewed in Section G of this report, and the Results and Discussion section of a recently submitted paper is presented below.

The second project is the reaction of D and H with silane, methyl silane, dimethyl silane, and trimethyl silane. To date the work on the methyl silanes is complete and the H and D with silane work is in progress. The completed work is also reviewed below.

(a) Experimental Investigation of Nonequilibrium Kinetic Isotope Effects in Chemically Activated Ethyl Radicals.

Results and Discussion

Ethyl radicals produced by the combination of H or D atoms with C_2H_4 or C_2D_4 are initially vibrationally hot and are referred to as being chemically activated. For the present systems the addition process yields ethyl radicals in their ground electronic state with calculable internal energy distributions. The primary addition step and the fate of the initially formed ethyl radicals for the four systems of interest in this study are:

The primed quantities refer to the isotopically substituted systems and single, double, and triple primed quantities will be used to refer to cases II, III, and IV, respectively. Secondary reactions of atoms, radicals, and isotopically exchanged ethylenes have not been included in the above mechanisms.

The subsequent reactions for each system affect the reaction stoichiometry, (i.e., the number of hydrogen or deuterium atoms consumed for each ethylene molecule removed from the system). For case I, the remaining steps in the mechanism have been presented³ and the major products of reaction were found to be methane, ethane, and methyl radicals. The absolute rate of formation of each product depends upon the initial reaction conditions. The proposed overall mechanism for the completely deuterated case is exactly the same as that for case I. The mechanisms for the mixed isotope systems, cases II and III, are similar but are more complex due to possibilities of isotopic mixing.

Although atomic hydrogen (deuterium) is consumed in secondary reactions of all four of the isotopically modified systems, reactant ethylene is not. The term "reactant ethylene" is used here to differentiate between initial reactant and any isotopically exchanged ethylene produced in cases II and III. With appropriate reaction conditions, the reactant ethylene molecules for each case are only consumed or regenerated in the first group

of reactions as shown above because secondary reactions involving reactant ethylene are negligible. This is an important aspect of these chemical activation systems because information about the initially formed vibrationally excited ethyl radicals may be obtained in each case by the observation of the rate of depletion of reactant ethylene during reaction.

Ethylene depletion may be observed mass spectrometrically with the flow system - TOFMS experiment and the apparent bimolecular rate constants can be determined from the experimental data in a straightforward fashion. In the $D + C_2D_4$ reaction, for example, the rate of removal of ethylene- d_4 is given by

$$-\frac{d[C_2D_4]}{dt} = k_{app}''' [D][C_2D_4] \quad (1)$$

If D atoms are in large excess relative to C_2D_4 , then $[D]$ will remain constant as C_2D_4 is consumed and equation (1) may be integrated to give

$$\ln [C_2D_4] = -(k_{app}''' [D]_0)t + \text{constant} \quad (2)$$

Thus, the kinetics are forced to be first order and the pseudo-first order decay constant is given by $k_{1st}''' = k_{app}''' [D]_0$. First order decay constants based upon observation of C_2D_4 depletion have been obtained as a function of $[D]_0$, with $[D]_0 = 20$ to $100 [C_2D_4]_0$. Three typical first order decay plots are shown in Fig. 1. At one particular total pressure, at least 5 or 6 first order decays are obtained. The first order decay constants are then plotted as a function of $[D]_0$. This plot results in

a straight line with a slope of k_{app}''' . The linear relationship between k_{1st}''' and $[D]_0$ is shown as a typical result in Fig. 2. The three solid points in Fig. 2 are from the decays in Fig. 1. The complete set of experiments is then repeated at different pressures, ranging from 1 to 5 torr for the flow reactor-TOFMS experiment.

The resultant apparent bimolecular rate constants, k_{app}''' , for the $D + C_2D_4$ reaction are listed in Table I along with the total pressures of the experiments. The rate constant is pressure sensitive, just as it is for the completely protonated case,^{3,5} and tends to increase with increasing pressure. Since these rate constants are determined from C_2D_4 decays under D-atom excess conditions where secondary reactions involving C_2D_4 are insignificant, the results correlate directly with the unit stoichiometric reaction. Consequently the pressure dependent rate constants, k_{app}''' , refer to the chemical activation and subsequent stabilization of ethyl-d₅ radicals for the overall process,

Apparent bimolecular rate constants for the $D + C_2D_4$ reaction have also been obtained with experiment B, the real-time Lyman- α photometric system. In this experiment, D atom consumption is observed during reaction with isolation conditions such that $[D]_0 \ll [C_2D_4]_0 \ll [He]$. With the use of Beer's law, pseudo-first order atom decay constants are obtained from oscilloscopic records of deuterium Lyman- α transmittances as a function of time. The decay constants for one particular pressure

are plotted as a function of initial ethylene- d_4 concentration and result in a linear plot. The slope of the line is the value of the rate constant, k_{exp} . Similar to the procedure used for the flow system experiments, the set of experiments is repeated as a function of pressure in order to determine the pressure dependence of k_{exp} .

The results of these experiments are listed in Table II. These rate constants are necessarily determined in C_2D_4 excess experiments by observation of D atom attenuation. Since the initial chemical activation reaction may result in the formation of reactive species which can also remove D atoms in secondary processes, the rate constant k_{exp} is more complex than that measured by observation of C_2D_4 consumption, k_{app} , in experiment A. The relationship between the two rate constants may be expressed as $k_{\text{exp}} = S k_{\text{app}}$, where S is the reaction stoichiometry factor.

The problem of stoichiometric effects due to secondary reactions of hydrogen atoms has been considered in detail in this laboratory for the completely protonated case.⁵ In that work, consideration of the four step sequence of chemical activation reactions in the proposed mechanism and specification of the rate constants for each step led to predicted stoichiometry factors after an iterative Runge-Kutta fourth order integration procedure. This procedure resulted in stoichiometry-corrected rate constants, $1/S(k_{\text{exp}})$, which could be identified with the unit stoichiometry rate constants for the initial chemical activation step. A similar procedure has been applied in the present work for the $D + C_2D_4$ reaction in order to extract the apparent bimolecular rate constants, k_{app} , from those obtained with experiment B. The predicted stoichiometry factors and the unit stoichiometric values of the rate constant, k_{app} , for the

chemical activation of ethyl-d₅ radicals are also listed in Table II. The stoichiometry-corrected rate constants in Table II may be compared with the unit stoichiometry values in Table I. For the same range of pressure, this two apparatus comparison of rate constants shows good consistency when the experimental errors in both sets of data are considered.

Comparison of these values of the apparent bimolecular rate constants with those for the $\text{H} + \text{C}_2\text{H}_4$ reaction shows that the $\text{D} + \text{C}_2\text{D}_4$ reaction is faster at low pressures. At one torr, for example, the value of the rate constant for the completely deuterated case is nearly twice that for the fully protonated case; rate constants for $\text{D} + \text{C}_2\text{D}_4$ continue to be larger than those for $\text{H} + \text{C}_2\text{H}_4$ up to 15 torr. This observation is due to a non-equilibrium inverse isotope effect and is discussed in a subsequent paper in terms of RRKM theory.¹⁶

Absolute rate constants for the $\text{D} + \text{C}_2\text{H}_4$ reaction in helium diluent which are obtained with the flow system-TOFMS experiment by the isolation method described above, are also presented in Table I. Rate constants for this chemical activation system were measured for both isolation conditions, $[\text{D}]_0 \gg [\text{C}_2\text{H}_4]_0$ and $[\text{C}_2\text{H}_4]_0 \gg [\text{D}]_0$. In the D-atom excess experiments, where C_2H_4 depletion is observed, the apparent bimolecular rate constant shows virtually no pressure dependence in the pressure range of 1 to 5 torr; its average value is $(7.63 \pm 0.07) \times 10^{-13}$ cc molecule⁻¹ sec⁻¹. This insensitivity to changes in pressure is totally different from that observed for the fully protonated or fully deuterated cases, both of which showed pressure dependence over the same pressure range. Since this pressure independent rate constant is measured by

observation of ethylene decays in atom excess experiments, the results correlate with the unit stoichiometric reaction, i.e., reaction 1 - 4.

In the C_2H_4 excess experiments, however, where D atom consumption is observed, the rate constants do appear to be pressure dependent. This behavior is attributed to secondary reactions of D atoms which affect the reaction stoichiometry and which may be pressure dependent. In this case the rate constant decreases with decreasing pressure and appears to converge to an average value of $(7.8 \pm 0.6) \times 10^{-13}$ cc molecule⁻¹ sec⁻¹ for the three lowest pressure values. A comparison of this average value with the pressure independent value obtained in the atom excess experiments shows that the rate constants for the two isolation conditions are very nearly identical at pressures below 2 torr. This observation will also be discussed in terms of mechanism.¹⁶

Apparent bimolecular rate constants for the $H + C_2D_4$ reaction in helium diluent were also obtained as a function of pressure with the flow system-TOFMS experiment. For this case, rate constants were obtained only by observation of C_2D_4 decays in atom excess experiments in order to isolate the unit stoichiometric values. Unlike the behavior observed for the $D + C_2H_4$ reaction, the rate constants for the $H + C_2D_4$ reaction exhibit a pressure dependence in the pressure region of 1 to 5 torr (see Table I).

After determining the unit stoichiometric values of the rate constants as a function of pressure for the mixed isotope cases, and observing that k_{app} for $D + C_2H_4$ is insensitive to changes in pressure while k_{app} for $H + C_2D_4$ is pressure dependent, it was of interest to study the reaction mechanisms and attempt to elucidate the observed behavior in each case.

In the $D + C_2H_4$ reaction the primary chemical activation step yields an excited ethyl-d₁ radical which may decompose by H- or D-atom rupture or become stabilized by collision with heat bath molecules (reactions 1' → 4'). For experimental conditions where $[D]_0 \gg [C_2H_4]_0$, secondary reactions of H atoms are negligible and only the following secondary processes need to be considered.

It is apparent that secondary processes for this mixed isotope case are much more complex than those of the completely protonated or completely deuterated cases due to possibilities of isotopic mixing. In addition to secondary reactions with isotopically exchanged ethylenes, D atoms may also react with any stabilized ethyl radical.

Similar to the mechanism for the $H + C_2H_4$ reaction,³ reaction (17') should be followed by C-C bond rupture which will yield a distribution of isotopically substituted methyl radicals. The methyl radicals may also react with atoms and exchange or become collisionally stabilized to form methane.

Furthermore, methyl radicals may recombine to form an excited ethane molecule which is lower in energy than those formed by reaction (17').³ This ethane species may then either decompose back to methyl radicals or be stabilized to yield ethane as a product.

The flow system-TOFMS experiment is well suited to study reaction mechanisms since absolute concentrations of reactants and products may

be observed directly as a function of reaction time. By observation of the product distribution during reaction, information concerning the relative importance of various steps in the proposed mechanism may be obtained.

Experimentally, product distribution profiles are obtained by scanning and recording the complete mass spectrum as a function of probe distance, while maintaining all other experimental conditions (i.e., reactant flow rates, flow velocity, pressure, etc.) as constant as possible. Data work-up for profile experiments includes mass peak height corrections to parent mass peaks for fragmentation patterns from higher massed species (discussed in the experimental section), specification of mass spectrometer sensitivities for the species observed during reaction, and calculation of the reaction time. Mass spectrometer sensitivities, defined by the ratio of concentration to mass peak height, for the species observed during reaction are determined immediately before and after each profile experiment as described previously.³ The sensitivity factors are then used to calculate absolute concentrations of species which appear during reaction from the observed mass peak heights. Sensitivity factors for C_2H_4 and C_2D_4 , for a particular profile experiment, were found to be approximately equal. Therefore, any partially deuterated ethylene observed during the reaction was assumed to have the same sensitivity factor. From lack of a good method for determining the sensitivity of methyl radicals, all C_1 products (methyl radicals and methanes) were assumed to have the same sensitivity factor. The C_1 sensitivity factor for each experiment was calculated as an average value for various reaction times from carbon mass balance expressions.¹⁷

Product distribution profiles were obtained for the $D + C_2H_4$ reaction in helium diluent at pressures of 1, 3, and 5 torr. For all profile experiments, isolation conditions were employed such that $[D]_0 \approx 20$ to $30 [C_2H_4]_0$ and secondary reactions of H atoms, relative to those of D atoms, could be neglected. Also, the conversion of reactant ethylene was limited to 50-70% in order to minimize fragmentation pattern corrections from any heavier ethylenes formed during reaction. Profile results for this case at pressures of 1 and 5 torr are shown in Figures 3A and 3B, respectively. The major products of the reaction are H, C_2H_3D , $C_2H_2D_2$, C_2HD_3 , and C_2D_4 . Only very small amounts of C_1 products (methyl radicals and methanes) were observed, even at 5 torr and longer reaction times. Essentially no C_3 or C_4 products were observed under the present experimental conditions. This observation confirms the earlier observation³ that radical-radical and radical-molecule reactions are unimportant in comparison to atom-radical and atom-molecule reactions. In addition, no HD was observed for any of the profile experiments. This observation indicates that atom-radical disproportionation and atom-molecule abstraction reactions are also unimportant in comparison to atom addition reactions for the conditions described.

Reference to Figure 3A, the $D + C_2H_4$ profile at 1 torr, shows that the initial rates of formation of H and C_2H_3D are approximately equal, and they should be according to the proposed mechanism (reaction 3'). As the reaction proceeds, C_2H_4 is consumed and H continues to increase, C_2H_3D levels off while $C_2H_2D_2$ begins to increase, and C_2HD_3 and small amounts of C_2D_4 build up gradually at later times. An important aspect of this profile is that the sum total of all ethylenes remains constant

throughout the time course of the reaction and their total concentration is approximately equal to the initial concentration of reactant ethylene. That is,

$$[C_2H_4]_0 \approx [C_2H_4]_t + [C_2H_3D]_t + [C_2H_2D_2]_t + [C_2HD_3]_t + [C_2D_4]_t$$

for any time t . Also, essentially no C_1 products are observed at 1 torr. In addition, all of the H observed can be accounted for by the following mass balance expression.

$$[H]_t \approx [C_2H_3D]_t + 2[C_2H_2D_2]_t + 3[C_2HD_3]_t + 4[C_2D_4]_t$$

At 5 torr total pressure, Fig. 3B, the profile is not much different from that obtained at 1 torr. The total concentration of all ethylenes is again nearly constant and only begins to drop off very late in the reaction. As the total concentration of ethylenes drops off, some C_1 products begin to appear. The C_1 products include methyl radicals (CH_2D , CHD_2 , and CD_3) and methanes (CH_2D_2 and CD_4) and are shown collectively as the larger solid circles in the profile. Since C_1 products are thought to be produced by secondary reactions of atoms with collisionally stabilized ethyl radicals, the absence of any significant amount C_1 formation indicates that very little stabilization occurs, even at 5 torr.

All of the experimental observations discussed above are consistent with the proposed mechanism for the $D + C_2H_4$ reaction. For this system, at pressures below 5 torr, the overall reaction appears to be a fast, sequential, isotopic exchange process which involves the formation of vibrationally excited ethyl radicals that undergo rapid unimolecular

decomposition by C-H bond rupture.

However, the situation is quite different for the other mixed isotope case, the $H + C_2D_4$ reaction. The proposed mechanism for this case is exactly analogous to that for the $D + C_2H_4$ reaction, except that H and D are interchanged for all species throughout the mechanism (reactions 5' - 21'), and all elementary steps and rate coefficients are referred to as double-primed quantities. Product distribution profiles for this system were also obtained in helium diluent at pressures of 1, 3, and 5 torr. Isolation conditions were again employed such that $[H]_0 \approx 20$ to 30 $[C_2D_4]_0$ for all profile experiments and the conversion of C_2D_4 was limited to 50-70%. Profile results for this case at pressures of 1 and 5 torr are shown in Figures 4A and 4B, respectively. The major products observed for this system are isotopically exchanged ethylenes (C_2D_3H , $C_2D_2H_2$, and C_2DH_3) and (unlike case II) an abundance of C_1 products (CH_2D_2 , CH_3D , CH_4 , CHD_2 , CH_2D , and CH_3). Deuterium atoms could not be observed without perturbing the experimental conditions (electron ionizing energy) because of the large mass 2 peak from molecular hydrogen. For this case (like case II) no HD was observed in any of the profile experiments, even with a hundred-fold increase in detection sensitivity. Also, no C_3 or C_4 products were observed and mass balance of all carbon was adequately accounted for by the observed ethylenes and C_1 products with the expression:

$$[C_2D_4]_0 \approx [C_2D_{4-m}H_m]_t + 2[CD_{4-m}H_m]_t, 0 \leq m \leq 4$$

Therefore, similar to that found for case II, only atom-molecule and atom-radical addition reactions appear to be important for this chemical activation system under the present conditions.

The $\text{H} + \text{C}_2\text{D}_4$ product distribution profile in Fig. 4A was obtained at 1 torr total pressure. Here again, the solid diamond shaped points represent the sum total of all ethylenes. Contrary to that observed for case II, the total concentration of ethylenes for this case decreases as the reaction proceeds and a significant amount of C_1 products are formed, even at 1 torr. At 5 torr, in Fig. 4B, the total amount of ethylene decreases to a greater extent, and the total concentration of C_1 products builds up markedly. These observations indicate that collisional stabilization is becoming the predominant channel for removing the vibrationally hot ethyl radicals in the $\text{H} + \text{C}_2\text{D}_4$ system and that unimolecular decomposition is becoming less important in the pressure range of 1 to 5 torr.

Information concerning the fate of the initially formed, chemically activated ethyl- d_1 and ethyl- d_4 radicals can also be obtained from the profile experiments. In the $\text{D} + \text{C}_2\text{H}_4$ reaction, for example, the initial chemical activation step (reaction 1') results in the formation of a vibrationally excited ethyl- d_1 radical which may be removed by three different modes (reactions 2' $\rightarrow$ 4'), two of which contribute to net depletion of reactant ethylene (unimolecular decomposition by H-rupture (D'_{H}) and collisional stabilization (S')). An evaluation of the relative importance of D'_{H} and S' can be made from an analysis of the product distribution profiles. For the chemically activated ethyl- d_1 radical, the value of the ratio $\text{S}'/\text{D}'_{\text{H}}$ may be obtained from the early stage of the reaction before any significant amount of ethylene- d_2 , -d_3 , or -d_4 has been formed. The initial rate of consumption of C_2H_4 is a measure of $\text{S}' + \text{D}'_{\text{H}}$, while the initial rate of formation of $\text{C}_2\text{H}_3\text{D}$ is only a measure of D'_{H} .

Therefore, the value of $(S' + D'_H)/D'_H$ may be estimated from the difference between the amount of C_2H_4 consumed and the amount of C_2H_3D formed in the initial stage of the reaction. From the profile experiments performed at total pressures of 0.96, 3.00, and 5.02 torr, the values of the ratio S'/D'_H were found to be $.02 \pm .015$, $.04 \pm .03$, and $.05 \pm .03$, respectively.

Similarly, for the $H + C_2D_4$ reaction, the two reaction channels which contribute to the net consumption of C_2D_4 are unimolecular decomposition of the hot ethyl- d_4 radical by D-rupture (D''_D) and collisional stabilization (S''). An evaluation of the relative values of S'' and D''_D may also be made from an analysis of the product distribution profiles. For the ethyl- d_4 system, the values of the ratio S''/D''_D are $.66 \pm .16$, $1.24 \pm .11$, and $1.69 \pm .25$ at total pressures of 0.95, 3.01, and 5.05 torr, respectively.

The present results may be compared to those of other workers who have used both absolute and relative techniques. Thus, Current and Rabinovitch^{10,11} (CR) obtained the ratio of ethyl- d_1 stabilization to decomposition by H rupture (S'/D'_H) at room temperature to be 0.023, 0.085, 0.098, and 0.215 at pure ethylene pressures of 0.15, 0.54, 1.00, and 2.55 torr, respectively. These workers have also found in the ethyl- d_3 system that the strong collisional deactivation efficiency of He relative to pure trans- $C_2H_2D_2$ is 0.26.¹² Work from this laboratory⁵ on the $H + C_2H_4$ system has yielded a strong collisional deactivation efficiency for He of $0.28 \pm .03$ relative to SF_6 . If both ethylenes and SF_6 have unit collision efficiencies, these results are consistent and allow the present S'/D'_H values to be compared with those of CR quoted above after appropriate

corrections for collision efficiency and collision frequency. Thus, 1 torr of ethylene should be equivalent to about 5 torr of He, and the present data at 0.96, 3.00, and 5.02 torr He (0.020 ± 0.015 , 0.04 ± 0.03 , and 0.05 ± 0.03 , respectively) should compare with the 0.15, 0.54, and 1.00 torr C_2H_4 data directly (0.023, 0.085, and 0.098, respectively).

Within experimental uncertainties, the agreement is good.

13
Turner and Cvetanovic (TC) have studied both isotopically mixed cases at somewhat higher pressures in a static system at room temperature. Thus, $D + C_2H_4$ was studied in D_2 diluent from 50-600 torr, and $H + C_2D_4$ was studied in H_2 diluent from 50-300 torr. In both systems the atom to ethylene ratio was small, and atom-radical reactions were negligible. The principle observation was the isotopic composition of the butanes. In the $D + C_2H_4$ system TC found that C_2H_4D , $C_2H_3D_2$, and C_2H_5 were all necessary to explain butane compositions. Also isotopic exchange persisted to high D_2 pressures. However, in the $H + C_2D_4$ system only C_2D_4H radicals were indicated from the butane composition, and no appreciable exchange occurred at pressures from 50-300 torr H_2 .

The present work supports the data of TC but offers alternative explanations for their observations. In the $D + C_2H_4$ system at 5 torr He, S'/D'_H is only 0.05 ± 0.03 . This suggests a short lifetime for $C_2H_4D^*$ with respect to H rupture. If the high pressure limit for this case is above 600 torr, then substantial mixing can still occur through reaction (3') even though stabilization may be competitive and, not only will C_2H_3D be a product but H atoms will also result. Under ethylene excess conditions H will add to ethylene and a substantial fraction of $C_2H_5^*$ will be stabilized. Also subsequent D with C_2H_3D reaction with partial stabilization can explain the presence of $C_2H_3D_2$ radicals. In the $H + C_2D_4$ system even at 5 torr He the S''/D''_D value is 1.69 ± 0.25 . In the work of TC the high pressure

limit may already be attained at 50-300 torr H_2 in which case the only important process is stabilization. This results in C_2D_4H exclusively in agreement with their observations.

In a study similar to that reported here, Toby and Schiff (TS)¹⁴ studied the room temperature $D + C_2H_4$ reaction in D_2 diluent in a flow reactor from 1 to 5 torr. Products were collected and analyzed for isotopic substitution. $[D]$ to $[C_2H_4]$ ratios ranged from 2.3 to 0.04. All possible isotopically substituted methanes, ethanes, and ethylenes were reported and methanes were the major product. These results would appear to contradict those presented in Figure 3 where little or no C_1 products are indicated. However, the difference in these two studies is in initial concentrations of reactants. The present study was carried out with a large excess of D whereas most of the experiments of TS were under stoichiometric or ethylene excess. According to the present results the D will rapidly react with ethylene and the predominate product, H, will attain higher concentrations than D after a short reaction time. H atoms will be removed by reactant C_2H_4 with the formation of stabilized C_2H_5 . C_2H_5 will then add either H or D and crack to two methyl radicals one of which may be isotopically substituted. C_2H_6 and C_2H_5D should then be the predominate ethanes, and TS report this to be the case. In addition to H atoms from reaction (3') the other product is deuterated ethylene. Thus, the suggestion of TS that C_2H_3D may arise from the atom-radical disproportionation, $D + C_2H_4D \rightarrow C_2H_3D + HD$, is not necessary. The observation in the present study of no HD as a product indicates that such a process does not occur.

Dodonov, et al.,⁸ also reported no HD formation in the $D + C_2H_4$ system. These workers also measured the temperature dependence (296-569°K), but

did not measure the pressure dependence of the apparent rate constant with their flow reactor-mass probe diffusion cloud technique. At 296°K and at 6.7 torr they report a value of 11.3×10^{-13} ($\pm 30\%$) cc molecule⁻¹ sec⁻¹ for the absolute rate constant. This is 50% higher than that reported here. These workers also investigated the $\text{H} + \text{C}_2\text{H}_4$ reaction, and the reported values are also 30-70% greater than those referenced in Table I.

The only other absolute determination for a mixed case is that of Braun and Lenzi (BL) for $\text{H} + \text{C}_2\text{D}_4$. They report values of 8.7×10^{-13} ($\pm 15\%$) and 10.0×10^{-13} ($\pm 15\%$) cc molecule⁻¹ sec⁻¹ at 29 and 75 torr respectively. As discussed above in conjunction with the work of TC, this reaction is likely to be in its high pressure limit above 50 torr. BL support this view.

All of the experimental conclusions which have been presented are also in agreement with theoretical considerations. These will be presented in a subsequent paper.¹⁶

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Table I

Absolute Rate Constants for $\text{H} + \text{C}_2\text{H}_4$, $\text{D} + \text{C}_2\text{H}_4$, $\text{H} + \text{C}_2\text{D}_4$, and $\text{D} + \text{C}_2\text{D}_4$ in Helium Diluent at $(297 \pm 1)^\circ\text{K}$. Results from the TOFMS Discharge-flow System.

System	Experimental Conditions	Pressure (torr)	$k_{\text{app}}^a \times 10^{13} \text{ (cc molecule}^{-1} \text{ sec}^{-1})$
I.	$\text{H} + \text{C}_2\text{H}_4$	(Table I of Ref. 3, Tables I, II, and IV of Ref. 5, and Table II of Ref. 15)	
II.	$\text{D} + \text{C}_2\text{H}_4$ $[\text{D}] \gg [\text{C}_2\text{H}_4]$	0.96	7.7
		1.27	7.6
		1.95	7.6
		2.96	7.6
		3.95	7.7
		5.00	7.6
	$[\text{C}_2\text{H}_4] \gg [\text{D}]$	1.25	7.2
		1.64	8.1
		1.76	8.0
		3.12	11.4
		4.16	12.1
III.	$\text{H} + \text{C}_2\text{D}_4$ $[\text{H}] \gg [\text{C}_2\text{D}_4]$	0.91	6.9
		1.94	7.6
		3.02	8.7
		3.96	9.3
		4.93	9.8
IV.	$\text{D} + \text{C}_2\text{D}_4$ $[\text{D}] \gg [\text{C}_2\text{D}_4]$	0.95	2.2
		1.97	2.7
		3.11	3.3
		3.96	4.2
		4.99	4.6

^aEstimated experimental error is $\pm 10\%$.

Table II

Stoichiometry-corrected Absolute Rate Constants for $D + C_2D_4$ in Helium Diluent at $(297 \pm 1)^\circ K$ with $[C_2D_4] \gg [D]$. Results from the Real Time Lyman- α Experiment.

Pressure (torr)	$k_{exp}^a \times 10^{13}$ (cc molecule ⁻¹ sec ⁻¹)	S	$k_{app} \times 10^{13}$ (cc molecule ⁻¹ sec ⁻¹)
0.98	4.0	1.9	2.1
2.44	6.6	1.9	3.5
3.00	6.6	1.7	3.9
5.27	8.2	1.5	5.5
7.43	6.8	1.3	5.3
10.31	7.1	1.2	5.9
15.18	7.8	1.2	6.5

^aEstimated experimental error is $\pm 15\%$.

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Figure Captions

Figure 1. Pseudo-first order ethylene-d₄ decays for D + C₂D₄ in helium diluent at 4.99 torr, 296°K, and a linear flow velocity of 1020 cm sec⁻¹. Plots of the mass peak height of C₂D₄ against probe distance for the isolation conditions:

$$[C_2D_4]_0 \ll [D]_0 \ll [He].$$

O, $[D]_0 = 1.23 \times 10^{14}$ atoms cc⁻¹; □, $[D]_0 = 1.70 \times 10^{14}$ atoms cc⁻¹; △, $[D]_0 = 4.89 \times 10^{13}$ atoms cc⁻¹.

Figure 2. Determination of k_{app}''' for D + C₂D₄ in helium diluent at 4.99 torr (same pressure, temperature, and flow velocity as in Fig. 1). Plot of the first order ethylene-d₄ decay constants against [D]. The three solid points are obtained from the first order decays shown in Fig. 1. Slope = $k_{app}''' = 4.58 \times 10^{-13}$ cc molecule⁻¹ sec⁻¹.

Figure 3. Concentration-time profiles for D + C₂H₄ at 296°K. O, C₂H₄; ▼, H; □, C₂H₃D; ○, C₂H₂D₂; △, C₂HD₃; ■, C₂D₄; ◆, total concentration of all ethylenes; ●, total concentration of C₁ products (discussed in text).

A. Total pressure = 0.96 torr; $[C_2H_4]_0 = 2.26 \times 10^{12}$ molecules cc⁻¹, $[D]_0 = 4.85 \times 10^{13}$ atoms cc⁻¹.

B. Total pressure = 5.02 torr; $[C_2H_4]_0 = 2.03 \times 10^{12}$ molecules cc⁻¹, $[D]_0 = 6.05 \times 10^{13}$ atoms cc⁻¹.

Figure 4. Concentration-time profiles for $\text{H} + \text{C}_2\text{D}_4$ at 296°K .

$\bigcirc$, C_2D_4 ; $\square$, $\text{C}_2\text{D}_3\text{H}$; $\bigcirc$, $\text{C}_2\text{D}_2\text{H}_2$; $\triangle$, C_2DH_3 ;

$\blacklozenge$, total concentration of all ethylenes; $\bullet$, total concentration of C_1 products (discussed in text).

- A. Total pressure = 0.95 torr; $[\text{C}_2\text{D}_4]_0 = 1.93 \times 10^{12}$ molecules cc^{-1} , $[\text{H}]_0 = 5.06 \times 10^{13}$ atoms cc^{-1} .
- B. Total pressure = 5.05 torr; $[\text{C}_2\text{D}_4]_0 = 2.49 \times 10^{12}$ molecules cc^{-1} , $[\text{H}]_0 = 6.43 \times 10^{13}$ atoms cc^{-1} .

Fig. 1

Fig. 2

Fig. 3

Fig. 4.

(b) The H and D Reactions with Mono-, Di-, and Tri-methyl Silanes

Experimental

The apparatus which was used has been described previously so no detailed description will be given. Experiments were carried out at room temperature in excess He in a discharge flow reactor. The reactor was poisoned with Drifilm and experiments were performed in both excess reactant and excess atom concentrations. Thus, pseudo-first order decays were measured. Under atom excess conditions, reactant decays were measured at four to six atomic concentrations. The decay constants were found to be linearly proportional to atom concentrations, and the slope of the k_{1st}^R vs. $[H]_0$ or $[D]_0$ graph is the apparent bimolecular rate constant, k_{app}^R . Similarly experiments in reactant excess were performed and first order decay constants based on atom attenuations were measured at four to six reactant concentrations. Again the slope of the linear $k_{1st}^{H(D)}$ vs. $[R]_0$ graph is the apparent bimolecular rate constant, $k_{app}^{H(D)}$.

Regardless of which reactant molecule was used, the presence of reactants of the type studied in this paper greatly increased the wall activity for atomic wall recombination. Thus, in the reactant excess cases, the extrapolated zero reactant decay constants ranged from 10 to 50 sec^{-1} depending on the frequency of the Drifilm poisoning process. In this case the first order decay constant is $k_w + k_{app}^{H(D)}[R]_0$, and the non-zero intercept value measures the wall recombination rate constant. The slope of $k_{1st}^{H(D)}$ vs. $[R]_0$ still gives $k_{app}^{H(D)}$, but unless the measurements are made at a variety of $[R]_0$ the inferred values for $k_{app}^{H(D)}$ will be greatly in error. Also in the H or D in excess experiments where attenuation of R is measured, stabilization of atom

concentrations is impossible even though atom concentrations exceed reactant concentrations by thirty to eighty. This observation might be interpreted as the presence of a very fast homogeneous reaction between atoms and silanes, but the rate of atom removal is not at all dependent on reactant concentration. The same attenuation in atom concentration is observed with any reactant concentration. The time it takes to establish the constant steady-state atom concentration at a particular dwell time varies with reactant concentration, but the level of atom concentration is the same regardless of the reactant concentration. This observation clearly suggests that the walls of the reactor are being treated with reactant and instabilities in atom concentration are caused by increased wall activity.

Reactant decay constants can still be measured in such a system if the decay is observed over a limited change in atom concentration. Thus, the results presented in this paper are obtained only over a 50% atomic concentration change, and the atom concentration is taken as the average of the initial and final dwell time values. Because of this troublesome wall problem, the rate constants in both atom excess and reactant excess systems are estimated to only be accurate to $\pm 20\%$.

In addition to rate constants measurements, complete mass spectra were obtained as a function of dwell time in both reactant excess and atom excess experiments. Products of the reactions have been identified and followed as a function of time, and thus, reaction profiles in the form of peak height vs. time have been obtained.

Dimethyl and monomethyl-silanes were obtained from PCR Inc. and trimethyl silane was obtained from Columbia Organic Chemicals Inc. All silanes were purified by bulb to bulb distillation, and the middle third was used. Purity

checks were routinely made by mass spectrometry. Research grade H_2 and D_2 (99.7% isotopically pure) were obtained from Air Products and Chemicals Inc. and Isomet Corporation and were used as received.

Results and Discussion

The room temperature rate constants which were measured are presented in Table I for the three methyl silanes with H and D in both atom excess and reactant excess experiments. No measurable differences in rate constants could be documented within experimental error with changes in total pressure. Also the constants obtained with reactant in excess are always larger than those obtained with atoms in excess. This indicates that a large stoichiometric correction is necessary for the reactant in excess experiments. This point is discussed further in connection with each reaction system.

In all cases the initial process is hydrogen abstraction from the reactant silane. As will be shown the abstracted hydrogen is bound to the silicon atom and not the carbon atom. This is observed as an increase in $m/e = 3$ due to HD formation in the D with silane studies. The subsequent reactions which occur are complicated and will be discussed separately in connection with each reaction system. The order of discussion below follows the order of complexity.

H and D with $(CH_3)_3SiH$:

$(CH_3)_3SiH$ depletion was observed in the presence of excess D concentration. The mass spectrum of $(CH_3)_3SiH$ at 19 ± 1 ev consists of $m/e = 73$ with silicon isotope peaks of 5% and 3% at 74 and 75. As is the case with all of the methyl silanes there are no appreciable parent peaks at the parent molecular mass ($m/e = 74$ in the case of $(CH_3)_3SiH$ for the most abundant isotope of silicon). The mass spectrum at 19 ± 1 ev also consists of major mass peaks

at 59 and 58 (intensities of 1.1 and .53 of $m/e = 73$, respectively). These fragmentation peaks are derived from the parent mass less CH_3 and CH_4 (or $\text{CH}_3 + \text{H}$). In the D in excess experiments the $m/e = 73$ (the parent mass less one) peak was chosen as a measure of reactant concentration. Also higher masses up to $m/e = 78$ were monitored as a function of dwell time and $58 \leq m/e \leq 60$ was observed. Very small but measurable concentrations of masses up to $m/e = 78$ were observed, but there was no appreciable relaxation up to the higher masses as a function of dwell time. That is $m/e = 74-78$ increased proportionately to one another. These peaks are undoubtedly due to deuteration of $(\text{CH}_3)_3\text{SiH}$ and must include deuteration in the methyl groups. Depletion of reactant $(\text{CH}_3)_3\text{SiH}$ was observed at $m/e = 73$, and, based on equal sensitivities for trimethyl silanes, the conversions to the deuterated compounds only amount to $\sim 3\%$ of the total loss of $m/e = 73$. Thus, the process which forms these compounds is minor in this system. Small but measurable amounts of CD_4 ($m/e = 20$) were observed as a product. The rate constant based on $m/e = 73$ depletion was found to be $0.3 \pm 0.2 \times 10^{-13}$ cc/molecule sec which indicates almost no reaction. The major process was observed in the $m/e = 58$ to 60 fragmentation peaks. For the same minor decrease in $m/e = 73$, the $m/e = 59$ peak decreases while the $m/e = 60$ increases substantially as shown in Figure 1. No higher mass products were observed, but H atoms as $m/e = 1$ were observed as a product of the reaction.

Reaction studies in excess H concentration were carried out where $m/e = 73$ was again taken as a measure of reactant concentration. Again only small depletion rates were observed, and the estimated rate constant is $(0.3 \pm 0.2) \times 10^{-13}$ molecules/cc sec as shown in Table I. Also small but measurable CH_4 was observed as a product at $m/e = 16$. On the basis of the above observations two alternative mechanisms can be proposed for the reaction.

The species marked with an asterisk are vibrationally hot and have to be considered as possibilities in the present low pressure work due to non-equilibrium effects. In mechanism I, reaction (-2) likely is negligible in comparison to reaction (3) since the Si-D bond is believed to be stronger by ~ 4 kcal/mole than the Si-C bond. The chemical activation function will then originate at the critical energy for reaction (-2) while the critical energy for reaction (3) will be lower lying by ~ 4 kcal/mole. Processes similar to reaction (-2) have then been neglected in mechanism II for the same reasons.

The observation of little depletion in both excess D and excess H in $m/e = 73$ while mixing in $m/e = 59$ and 60 is substantial in the D reaction, suggests that most of the reaction in this case is due to reactions (2) or (2') followed by stabilization (ω or ω'). If these processes were the only

important processes then re-formation of parent compound would occur exclusively in the H in excess system and no reactant depletion would be observed. The rate constant for depletion is, however, $(0.3 \pm 0.2) \times 10^{-13}$ cc/molecule sec, and this can be attributed to decomposition through methyl cracking (reactions (3) or (3')) in the D system). The presence of CH_4 as products in these atom excess systems confirms this observation as will be discussed below.

Stabilization is the major process and results in the production of either $(\text{CH}_3)_3\text{SiD}$ or $(\text{CH}_3)_2\text{SiH}(\text{CH}_2\text{D})$ in the D system depending on whether mechanism I or II is invoked. If $(\text{CH}_3)_2\text{SiH}(\text{CH}_2\text{D})$ is formed, the parent less one value for m/e (i.e. 73) should decrease for the reactant molecule and $m/e = 74$ should increase substantially. As discussed above only small conversions to highly deuterated trimethyl silanes are observed. This would indicate that mechanism II is unimportant. On the other hand, the assertion that $m/e = 73$ in the reactant molecule is due only to $(\text{CH}_3)_3\text{Si}^+$ ions, leads to the conclusion that this same molecular mass will result if $(\text{CH}_3)_3\text{SiD}$ is ionized. Also the observation of large changes in $m/e = 59$ and 60 is understandable since these are derived from parents less CH_3 . Thus, a good measure of reactant trimethyl silane and product trimethyl silane- d_1 are $m/e = 59$ and 60, respectively as shown in Figure 1.

Decay constants can then be obtained for $m/e = 59$ depletion in the D in excess system, and these yield a value for reactant depletion of $(1.7 \pm 0.2) \times 10^{-13}$ molecule/cc sec as indicated in Table I. This value then refers only to the stabilization process. As discussed above the total trimethyl silane concentration ($m/e = 73$) depletes with a rate constant of $(0.3 \pm 0.2) \times 10^{-13}$ cc/molecule sec due to methyl cracking. Thus, the total rate constant

for both stabilization and decomposition is $(2.0 \pm 0.4) \times 10^{-13}$ cc/molecule sec.

Mechanism I with the back reaction (-2) neglected then explains the observations. As will be discussed later in conjunction with the other methyl silane systems, the dimethyl silyl radicals which are produced in reaction (3) then react rapidly with D, and another methyl is cracked out. This scheme is analogous to reaction (2) followed by reaction (3) for trimethyl silyl (i.e. it goes through a chemically activated vibrationally hot species), but there is no evidence that stabilization (i.e. reaction (w)) can take place at the low pressure of these studies for dimethyl silyl. The overall process is then:

There is also no evidence for monomethyl silyl stabilization. The overall process following reaction (4) is:

In the D in excess system the methyl radicals from reactions (3), (4), and (5) rapidly exchange again through a chemical activation scheme. The overall processes are:

Thus, a distribution of deuterated methyl radicals is formed which depends on the D atom concentration, and H atoms are formed as a product which agrees

with observation. The deuterated methyl and silyl radicals will stabilize with difficulty (again through a chemical activation scheme) at the low pressures of these experiments,

(overall processes)

and recombination of methyl and any type of silyl radical, which is highly favored from a chemical activation viewpoint, will likely be partially competitive even with small radical concentrations.

(overall process)

Reaction (9) predicts CD_4 , and this is observed as a product; reaction (10) predicts SiD_4 , and this is observed as a product; and reaction (11) predicts mono-, di-, tri-, and tetra-deuteromethyl silanes as products. Of these possibilities deuterated trimethyl silanes are observed as minor products. Mono and dimethyl silanes are impossible to observe in small concentrations due to m/e peak interferences. No clear evidence was obtained to confirm tetramethyl silanes as a product.

Even though reactions (9) and (10) are not favored from a chemical activation viewpoint, these reactions are the major removal processes for methyl and silyl radicals at the conditions of these experiments (high [D]). Thus, we conclude that this system undergoes two overall processes in D in excess:

Both processes follow reaction (1) which is rate controlling. The D in excess rate constant for reactant depletion due to reaction (1) is, therefore, $(2.0 \pm 0.4) \times 10^{-13}$ cc/molecule sec.

In the reactant in excess experiments the measured rate constants based on D and H atom depletion are $(5.0 \pm 0.7) \times 10^{-13}$ and $(9.1 \pm 0.8) \times 10^{-13}$ cc/molecule sec, respectively. In all experiments the D and H atom concentrations ranged from 2 to 6×10^{12} atoms/cc. It is likely that the fast sequential atomic cracking scheme which gives CH_3 (reactions (2) and (3), (4), and (5)) is occurring. The resulting CH_3 and SiD_3 radicals do not appreciably recombine as discussed previously, and we envision these radicals as simply stabilizing with D atoms perhaps homogeneously or on the walls of the reactor. No firm evidence from product analysis could be obtained due to mass peak interference except that HD was definitely a product of the reaction. Thus, in the reactant in excess experiments the overall process for the D reaction is process (S) and process (D').

A rate constant for D depletion based on process (S) gives $2 k_1 (\omega/k_3 + \omega)$ in the steady state approximation while that based on process (D') gives $8k_1 (k_3/k_3 + \omega)$. As discussed previously in the D in excess experiments, $k_1 (\omega/k_3 + \omega) = (1.7 \pm 0.2) \times 10^{-13}$ cc/molecule sec, and $k_1 (k_3/k_3 + \omega) = (0.3 \pm 0.2) \times 10^{-13}$ cc/molecule sec. Thus, a value for the D depletion rate constant of $(5.8 \pm 2.0) \times 10^{-13}$ cc/molecule sec is inferred, and the

measured value is $(5.0 \pm 0.7) \times 10^{-13}$ cc/molecule sec. This is in adequate agreement.

The factors which correspond to processes (S) and (D') in the H atom depletion experiments are also 2 and 8, respectively. The measured rate constant in the H in excess experiments is $(0.3 \pm 0.2) \times 10^{-13}$ cc/molecule sec, and this is due to decomposition only. Thus, a value of $(2.4 \pm 1.6) \times 10^{-13}$ cc/molecule sec is inferred for the decomposition channel in the reactant in excess experiments. This leaves $\frac{1}{2} \{ (9.1 \pm 0.8) - (2.4 \pm 1.6) \} \times 10^{-13}$ cc/molecule sec for the stabilization channel. Thus, we infer a value for the abstraction rate constant in the H reaction with trimethyl silane of $\{ (3.35 \pm 1.20) + (0.3 \pm 0.2) \} \times 10^{-13}$ cc/molecule sec or $(3.65 \pm 1.40) \times 10^{-13}$ cc/molecule sec. This value is entered in Table II.

H and D with $(\text{CH}_3)_2\text{SiH}_2$:

$(\text{CH}_3)_2\text{SiH}_2$ depletion was observed in the presence of excess D concentrations. The 19 ± 1 ev mass spectrum of $(\text{CH}_3)_2\text{SiH}_2$ consists of major mass peaks at $m/e = 59, 58, 45$, and 44 with relative intensities of 1.0, 1.0, 0.42, and 0.98, respectively. Small but observable deuterated dimethyl silanes were observed as products. As in the trimethyl silane case, however, the processes which form these compounds is minor, HD ($m/e = 3$), CD_4 ($m/e = 20$), and SiD_4 ($m/e = 34$) were observed as products. All of the major mass peaks ($59, 58, 45$, and 44) decreased with an increase in dwell time, and first order decay constants based on attenuation of any of these peaks gave the same value within experimental error. Particular attention was given to the growth of $m/e = 46$ with $m/e = 45$ decay. The increase of $m/e = 46$ was negligible and could be interpreted as fragmentation of the minor deuterated dimethyl silanes. No large decrease in the parent molecular mass less CH_3

accompanied by a large increase in the parent- d_1 less CH_3 was observed. This case is clearly different from trimethyl silane. There is no evidence for stabilization of dimethyl silane- d_1 after initial abstraction and D addition. Instead the channel for decomposition is clearly favored. The mechanism which agrees with all of the observations is:

In the D in excess experiments the methyl and silyl- d_2 radicals rapidly exchange as in reactions (6), (7), and (8). These partially and totally deuterated radicals can give rise to minor buildup of deuterated tri-, di, and monomethyl silanes as in reaction (11), but their predominant fate in excess D is recombination (reactions (9) and (10)) to form SiD_4 and CD_4 . Both products are observed. Also higher mass observations indicate the formation of deuterated trimethyl silane in minor amounts.

Thus, the only process of importance is decomposition, and the overall process in excess D is:

Rate constants based on reactant depletion (as $m/e = 59, 58, 45, \text{ or } 45$) refer to the rate controlling reaction which is reaction (12). The value obtained is $(1.4 \pm 0.2) \times 10^{-13}$ cc/molecule sec. Similarly, the value obtained in the H in excess experiments is $(4.1 \pm 0.9) \times 10^{-13}$ cc/molecule sec, and this value refers to the abstraction rate constant. The process in the latter case is similar to that of process (D_1) only CH_4 and SiH_4 are predicted to be products. Both are observed at $m/e = 16$ and 31 , respectively.

2

Results were also obtained in the reactant in excess systems. Following the conclusions made in connection with the trimethyl silane cases that H and D concentrations are sufficiently small that mono-deuteration only occurs with free methyl and silyl radicals perhaps on the wall, the reactant in excess overall process is:

The measured rate constant based on D depletion is $(11.8 \pm 1.8) \times 10^{-13}$ cc/molecule sec, and a value one sixth of this or $(2.0 \pm 0.3) \times 10^{-13}$ cc/molecule sec should be the rate constant of the rate controlling reaction (12). As stated previously the value obtained in D excess is $(1.4 \pm 0.2) \times 10^{-13}$ cc/molecule sec, and the agreement is adequate. Process $(D_1)'$ for the H depletion experiments also shows that 6 H atoms are used up for one dimethyl silane. The measured value in the reactant in excess experiments with H is $(25 \pm 2) \times 10^{-13}$ cc/molecule sec, and this gives an inferred value for the H atom abstraction rate of $(4.3 \pm 0.3) \times 10^{-13}$ cc/molecule sec in good agreement with the previously stated value of $(4.1 \pm 0.9) \times 10^{-13}$ cc/molecule sec obtained in H excess. These values are listed in Table II.

H and D with CH_3SiH_3 :

This system is exactly similar to dimethyl silane. No evidence was found for stabilization. The reaction goes entirely through a decomposition channel after the initial abstraction. In the D in excess experiments the overall process is

The rate constant for reactant depletion is measured to be $(3.0 \pm 0.8) \times 10^{-13}$ cc/molecule sec. The H in excess value is $(11.5 \pm 2.0) \times 10^{-13}$ cc/molecule sec.

By analogy with the other systems the reactant in excess overall process is modified to:

The value obtained from D depletion experiments is $(12.5 \pm 1.8) \times 10^{-13}$ cc/molecule sec which yields a value of $(3.1 \pm 0.5) \times 10^{-13}$ cc/molecule sec in excellent agreement with the value from D in excess. Process (D_2') also suggests a value of 4 for the stoichiometry coefficient for the H depletion with reactant in excess experiments. The measured value of $(46 \pm 8) \times 10^{-13}$ cc/molecule sec which gives a value $(11.5 \pm 2) \times 10^{-13}$ cc/molecule sec in excellent agreement with the H in excess value previously given. These values are also listed in Table II.

As further evidence that abstraction in these systems is from the hydrogen bound to the silicon atom, small concentrations of $m/e = 90, 89, 88, 87,$ and 86 in ratios of $1.0, 0.9, 0.9, 0.4,$ and $0.6,$ respectively were observed in both reactant in excess systems with D and H. The spectrum was identical in both systems and was a product of the reaction. We suggest that this spectrum is due to the dimer of methyl silyl radicals, $(CH_3)_2H_4Si_2$. Production rates were minor and do not affect the stoichiometry arguments made above.

Table I

Rate Constants for H and D with Methyl-silanes at Room Temperature in Excess

Atoms and Reactants

Reactant	P(torr)	k_{app}^H ^{a,b}	P(torr)	k_{app}^D ^{a,b}	P(torr)	$k_{app}^{CH_3SiH_3}$ ^{a,c}	P(torr)	$k_{app}^{CH_3SiH_3}$ ^{a,d}
$(CH_3)_2SiH_3$	3	47 ± 9	1	14 ± 2	3	11.5 ± 2.0	3	3.0 ± 0.8
	3	45 ± 5	3	10.6 ± 1.2				
			5	13 ± 3				
$(CH_3)_2SiH_3$	3	25 ± 2	3	10 ± 1.0	3	4.1 ± 0.9	3	1.4 ± 0.2
			3	13.5 ± 1.0				
$(CH_3)_3SiH_3$	3	8.9 ± 0.7	3	5.7 ± 0.8			3	$(1.7 \pm 0.2) +$
	5	9.3 ± 0.9	5	4.3 ± 0.9	3	0.3 ± 0.2		$(0.3 \pm 0.2) =$ 2.0 ± 0.4

(a) Units are in 10^{13} cc/molecule sec

(b) Obtained with reactant in excess

(c) Obtained with H in excess

(d) Obtained with D in excess

Table II
Room Temperature Abstraction Rate
Constants for H and D with
Methyl Silanes

Reaction	$k_{\text{abs}} \times 10^{13}$ (cc/molecule sec)
H + CH ₃ SiH ₃	11.5 ± 2.0 ^a 11.5 ± 2.0 ^b
D + CH ₃ SiH ₃	3.0 ± 0.8 ^a 3.1 ± 0.5 ^b
H + (CH ₃) ₂ SiH ₂	4.1 ± 0.9 ^a 4.3 ± 0.3 ^b
D + (CH ₃) ₂ SiH ₂	1.4 ± 0.2 ^a 2.0 ± 0.3 ^b
H + (CH ₃) ₃ SiH	3.65 ± 1.4 ^b
D + (CH ₃) ₃ SiH	2.0 ± 0.4 ^a

(a) measured

(b) inferred (see text)

■ $m_e = 60$

● $m_e = 59$

◊ $m_e = 34$

▲ $m_e = 20$

Experiment F
Further Hg(3P_1) Quenching Studies

Introduction

Recently, Michael and Suess reported new experiments on the quenching of Hg(3P_1) by a variety of quenching gases. This work was also a topic of discussion in last year's Annual Progress Report (COO-3242-7). The work involved the classical type measurement of phosphorescence as a function of quencher pressure. Stern-Volmer analysis together with the known emissive lifetime of Hg(3P_1) yielded total bimolecular quenching rate constants, k_Q . The usual cross sections were calculated from the kinetic theory of gases expression,

$$\sigma_Q^2 = k_Q \left(8\pi RT \left(\frac{M_{Hg} + M_Q}{M_{Hg} M_Q} \right) \right)^{-\frac{1}{2}} \quad (1)$$

The essential conclusion of Michael and Suess was that the currently accepted scale of cross sections is low by about 25%. The reason this result is to be preferred is that Michael and Suess showed that most earlier studies improperly accounted for radiation imprisonment. The mercury opacity in Michael and Suess' experiments was purposely kept low so as to eliminate the necessity of a correction. Even so the real to natural lifetime ratio could have been as high as ~ 1.10 which would mean that the reported cross sections could be about 10% too high.

The present work, which is a continuation of that of Michael and Suess, was undertaken to test the results of Michael and Suess. In particular the mercury opacity was kept even lower in the present work

In the paragraphs to follow the results of these studies will be presented.

Results

A single quenching experiment consisted of monitoring the changes in transmitted and emitted radiation intensities following removal of a low-temperature bath from the cold trap. Mercury atoms then diffused into the photolysis cell which already contained a given pressure of quenching gas or was at high vacuum (0 torr quenching gas). The phototube output (i_t) was proportional to the transmitted intensity. It decreased with an increase in mercury vapor pressure due to the electronic excitation of mercury atoms by photons of the incident beam. The photomultiplier output (i_f) was proportional to the emitted intensity. It increased with an increase in mercury vapor pressure due to the isotropic emission of photons by excited mercury atoms which were not first quenched by molecules of the quenching species. The data collected in a single experiment was plotted as i_t versus i_f . The useful information obtained from this plot was the slope i_t/i_f . In a series of quenching experiments at different pressures of quenching gas, the slope was found to become more negative with increasing quencher pressure due to the decrease in emission intensity attributable to collisional quenching of mercury (6^3P_1).

The slope of the i_t versus i_f plot was found to be linear at high transmittance. The slope began to curve at high mercury vapor pressure (low transmittance) due to an end-on effect together with the complications of radiation imprisonment. The end-on effect became significant at high concentrations of mercury vapor because absorption of the incident beam of radiation began to occur sufficiently close to the front window of the photolysis cell that the proportion of emitted radiation detected by the photomultiplier became smaller than the constant proportion detected over a wide range of lower mercury vapor pressure.

Approximate calculations reported by Suess for the increase in lifetime of electronically excited mercury atoms in this photolytic apparatus indicate that radiation imprisonment could be assumed negligible. As a result of estimates based on Einstein's diffusion equation, Suess also reports that the diffusion of mercury vapor throughout the photolysis cell can be considered instantaneous in comparison with the run time of 2 minutes.

Only regions of i_t versus i_f plots with transmittance exceeding 90% were employed for determination of the slopes, although linearity extended to well below 80%. Because the intensity of the incident beam equals the sum of the absorbed and transmitted intensities, the slope i_t/i_f of the data plots equals the negative of i_a/i_f . The proportionality of the monitored photocurrents with the radiation intensities which holds at low mercury vapor pressure is given by equation (2),

$$\frac{i_a}{i_f} = C \cdot \frac{I_a}{I_f} \quad (2)$$

This relationship permitted the slopes from data plots which were determined at a number of quencher pressures to be used in constructing a modified Stern-Volmer plot,

$$\frac{i_a}{i_f} = C \left(1 + \frac{k_Q}{k_f} [Q] \right). \quad (3)$$

The slope-to-intercept ratio of the linear plot of i_a/i_f versus $[Q]$ provided the ratio of k_Q/k_f . The bimolecular quenching rate constant k_Q and the quenching cross section σ_Q^2 were calculated from the ratio k_Q/k_f as described earlier.

Table II presents the i_a/i_f values which were determined at various pressures of quenching gas for each of eight quenching species. The i_a/i_f

value for each experiment is the least squares fit of the slope in the linear region. The reported values of i_a/i_f represent the average of the least squares slopes from three or four experiments performed at the same pressure. The uncertainty of each reported i_a/i_f value represents the standard deviation obtained from the residuals from the mean.

The i_a/i_f values were least squares fit to a straight line as a function of quencher pressure $[Q]$ with each point weighted as the inverse of the square of the standard deviation. These Stern-Volmer plots are presented as Figures 1, 2 and 3. The slope-to-intercept ratio provides the value k_Q/k_f . In calculating the bimolecular quenching rate constant k_Q , a value of 1.14×10^{-7} sec. was used for the lifetime of mercury (6^3P_1). The quenching cross-section was calculated from equation (1). The experimentally determined quenching rate constants and cross sections are presented in Table III. The uncertainty reported for each value represents the standard deviation calculated with the standard deviations in the slope and intercept values from the least squares fit.

Table II: Photocurrent Ratio (i_a/i_f) as a Function of Quenching Gas Pressure

<u>H₂</u>		<u>D₂</u>	
<u>P_Q (torr)</u>	<u>$i_a/i_f \times 10^4$</u>	<u>P_Q (torr)</u>	<u>$i_a/i_f \times 10^4$</u>
0.	.80 ± .04	0.	1.46 ± .23
0.	.93 ± .08	.14	1.77 ± .22
.11	1.04 ± .09	.35	2.29 ± .19
.21	1.18 ± .07	.50	2.38 ± .38
.33	1.55 ± .18	.75	2.99 ± .28
.40	1.78 ± .08	.94	3.29 ± .23
.48	1.67 ± .19		
.61	1.89 ± .04		
.76	2.09 ± .20		
.96	2.50 ± .20		

Table II (continued)

<u>HD</u>		<u>C₃H₆</u>	
<u>P_Q (torr)</u>	<u>i_a/i_f × 10⁴</u>	<u>P_Q (torr)</u>	<u>i_a/i_f × 10⁴</u>
0.	1.62 ± .16	0.	1.77 ± .16
.16	1.85 ± .16	.28	2.33 ± .12
.35	2.27 ± .59	.40	2.81 ± .20
.49	3.12 ± .87	.56	3.10 ± .11
.61	3.17 ± .75	.75	3.90 ± .10
.83	3.85 ± .45	.95	4.49 ± .18

<u>1-C₄H₈</u>		<u>1-C₅H₁₀</u>	
<u>P_Q (torr)</u>	<u>i_a/i_f × 10⁴</u>	<u>P_Q (torr)</u>	<u>i_a/i_f × 10⁴</u>
0.	1.96 ± .06	0.	3.84 ± .17
.18	3.15 ± .18	.23	4.55 ± .22
.32	3.44 ± .12	.41	5.03 ± .05
.44	3.96 ± .64	.57	5.95 ± .20
.65	5.27 ± 1.31	.75	7.22 ± .74
.84	6.00 ± .72	.92	7.59 ± .07

Table II (continued)

<u>C₂H₂</u>		<u>C₄H₆</u>	
<u>P_Q (torr)</u>	<u>i_a/i_f × 10⁴</u>	<u>P_Q (torr)</u>	<u>i_a/i_f × 10⁴</u>
0.	.83 ± .08	0.	.55 ± .02
.14	1.18 ± .20	0.	.56 ± .06
.27	1.59 ± .20	.22	.86 ± .03
.39	1.90 ± .22	.40	1.02 ± .05
.48	2.01 ± .12	.58	1.18 ± .20
.61	2.12 ± .23	.75	1.28 ± .04
.67	2.21 ± .08	.95	1.66 ± .23
.77	2.51 ± .44

Table III: Quenching Rate Constants and Cross Sections

<u>Q</u>	<u>$k_Q \times 10^{10}$ (cc molecule⁻¹ sec⁻¹)</u>	<u>σ_Q^2(A²)</u>
H ₂	5.48 ± .21	9.8 ± .4
D ₂	3.42 ± .21	8.6 ± .5
HD	4.59 ± .50	10.0 ± 1.1
C ₃ H ₆	5.02 ± .54	37.6 ± 4.0
1-C ₄ H ₈	6.57 ± .48	55.3 ± 4.1
1-C ₅ H ₁₀	3.80 ± .35	34.8 ± 3.2
C ₂ H ₂	6.45 ± .56	39.4 ± 3.4
C ₄ H ₆	4.78 ± .36	39.7 ± 2.9

G. Experiment G

Calculations

Introduction

During the past year continuing RRKM theoretical calculations have been carried out. The results for the $H + C_2H_4$ with deuterated variations are now complete. Correlations have been made with experimental results (see experiment E), and they are extremely satisfactory. The second project, which is partially complete, is a theoretical analysis of the $H + C_2H_2$ system with deuterated variations. The results are available from the work of Dr. David G. Keil from these laboratories. In the paragraphs to follow the progress on both of these projects will be presented.

(a) Theoretical RRKM Calculations on $H + C_2H_4$ and Deuterated Variations.

The appropriate rate expressions for reactant ethylene depletion in the four chemical activation systems are all similar and are based upon the Rice-Ramsperger-Kassel-Marcus (RRKM) theory of unimolecular reactions.^{8,9} In case I, for example, an expression for the rate of C_2H_4 consumption may be obtained from the chemical activation mechanism⁶ if strong collisional deactivation is assumed, and if the concentration of $C_2H_5^*$ is assumed to be in steady state. The resulting expression is,

$$-\frac{d[C_2H_4]}{dt} = k_1 [H][C_2H_4] \int_{E_{OH}}^{\infty} \frac{\omega f(E)}{k_{EH} + \omega} dE, \quad (1)$$

where $f(E)$ is the normalized distribution function for formation of excited ethyl- d_0 radicals, E_{oH} is the critical energy with which $C_2H_5^*$ can decompose; k_{EH} is the energy-dependent, specific rate constant for decomposition of $C_2H_5^*$ by C-H bond rupture, and ω is the collision frequency of an excited ethyl radical with heat bath molecules. Thus, the apparent bimolecular rate constant for case I is:

$$k_{app} = k_1 \int_{E_{oH}}^{\infty} \frac{\omega f(E)}{k_{EH} + \omega} dE \quad (2)$$

Similarly, for cases II, III, and IV, the unit stoichiometric expressions for the apparent bimolecular rate constants are given by equations (3), (4) and (5), respectively.

$$k'_{app} = k'_1 \int_{E'_{oD}}^{\infty} \frac{(k'_{EH} + \omega') f'(E)}{(k'_{EH} + k'_{ED} + \omega')} dE \quad (3)$$

$$k''_{app} = k''_1 \int_{E''_{oH}}^{\infty} \frac{(k''_{ED} + \omega'') f''(E)}{(k''_{EH} + k''_{ED} + \omega'')} dE \quad (4)$$

$$k'''_{app} = k'''_1 \int_{E'''_{oD}}^{\infty} \frac{\omega''' f'''(E)}{k'''_{ED} + \omega'''} dE \quad (5)$$

where zero, one, two, and three primes are referring to cases I, II, III, and IV, respectively.

For non-unit stoichiometric rate constants (those based on atom decays under ethylene excess conditions), the overall stoichiometry number multiplies the collision frequency in the numerator of equations (2)-(5). Thus, in the limit of zero pressure, rate constants obtained from atom decays should approach those obtained from reactant ethylene decays. This is observed for case II,⁷ the $D + C_2H_4$ reaction.

The pertinent formulas for calculation of $f(E)$ and k_{Ei} require a knowledge of the sum of states for the activated complexes and the density of states for the excited radicals. In addition, the energetics of the reaction under consideration must be known. The procedure for calculation is well known,⁹ and the formulas and procedures used in the present study have been given previously.⁶

For each of the four ethyl radical systems, application of the theory requires specification of molecular models for the ethyl radicals and for the activated complexes. Model specification involves assignment of geometric configurations for calculation of principal moments of inertia and assignment of vibration frequencies to the active internal degrees of freedom for computation of sums and densities of states. A value must also be assigned to the critical energy E_{oi} . This is the minimum excess internal energy, above the zero-point, of an excited ethyl radical required for a particular decomposition mode, i . In addition to these parameters, the collision diameters for the ethyl radicals and third body gases must be specified in order to calculate the collision frequency, ω .

Instead of separately adjusting the models to fit the theoretical calculations to the experimental data in each of the four cases, a different approach was used. The model parameters for the completely protonated system were adjusted and refined until the best overall agreement was obtained between theory and experiment for both chemically and thermally activated ethyl- d_0 radicals. The experimental data used for final parametric assignments were obtained from seven different

sources^{3,5,10-12} and include a broad range of pressure (0.3 to 600 torr) and temperature (296-913°K). The calculational parameters for the other three cases were then derived from the successful models of the fully protonated system in a totally consistent manner. Since isotopic substitution has no effect on the electron distribution or potential energy surface for a molecule, and hence no effect on the ground state geometry or the force constants for vibration, models for radicals and complexes, zero-point energy differences, and critical energy differences may be obtained for the isotopically substituted cases which are consistent with all of the final parametric assignments of the completely protonated case. Consistency between models is insured with the Teller-Redlich product rule.¹³ Hence the molecular models and critical energies for all of the isotopically modified systems are based entirely upon the agreement between theory and experiment for the C_2H_5 system. This method of approach to parameter assignments for the deuterated versions involves no new adjustable parameters and should provide a rigorous test for several aspects of the RRKM theory. Failure to fit all of the experimental data in each case by a common molecular model should signify a deficiency of either the model or the theory.

Molecular Models

All ethyl radicals are considered to have identical structure. The complexes are also considered to have exactly the same geometrical configuration in each case. The vibration frequencies of the models

are obtained by application of the group frequency method of Pitzer.¹⁴

Frequencies characteristic of methylene and methyl groups are based upon the reported fundamentals for ethylene¹⁵ (C_2H_4 and C_2D_4) and ethane¹³ (C_2H_6 and C_2D_6), respectively. All of the genuine vibrations of the radical and complex are considered to be active degrees of freedom.

Internal rotation about the C-C bond of the ethyl radicals is assumed to be free rotation and is considered as an active degree of freedom. The reduced moment of inertia for internal rotation is calculated with the assumption that each radical consists of two coaxial symmetric tops.

The same assumption was made by MS⁶ and RS.⁸ Although this is a simplifying approximation, the actual asymmetry should not alter the energy level density significantly for rate calculation purposes.¹⁶

Case I: The models for C_2H_5 and $C_2H_4 \cdots H^\ddagger$ in the present study are similar to those proposed previously by MS and by Rabinovitch and co-workers.⁸

The radical consists of a planar methylene group, with regular trigonal bond angles, which is bonded to a methyl group, with tetrahedral bond angles.

The bond lengths for C_2H_5 are those given by Purnell and Quinn:¹⁷

1.08 Å for C-H of the methylene group, 1.107 Å for C-H of the methyl group, and 1.507 Å for the C-C bond. Vibration frequencies for C_2H_5 are derived from a combination of the fundamentals for C_2H_4 and C_2H_6 . A representative frequency for each type of motion is calculated from the geometric mean as suggested by Rabinovitch *et al.*¹⁸ For the methyl group, there are

3 C-H stretches at 2961 cm^{-1} , 3 H-C-H deformations at 1440 cm^{-1} , and 2 over-all bending modes characteristic of C_2H_6 at 974 cm^{-1} . The methylene group consists of 2 C-H stretches at 3047 cm^{-1} , 1 H-C-H in-plane scissoring mode at 1392 cm^{-1} , 1 in-plane over-all bending mode at 1001 cm^{-1} , and 1 out-of-plane bending mode at 485 cm^{-1} . The latter frequency and the $\text{H}_2\text{C}-\text{CH}_3$ stretching frequency (1050 cm^{-1}) are taken from the calculations of Purnell and Quinn.¹⁷ For convenience in tabulation, the assigned frequencies are grouped further: 2961 (3) with 3047 (2), 1440 (3) with 1392 (1), and 1001 (1) with 1050 (1). The geometric means are listed in Table I.

In agreement with previous studies,^{6,8} $\text{C}_2\text{H}_4\cdots\text{H}^\ddagger$ is considered to be a "loose" complex. Since the H atom is thought to be very loosely bound in the transition state, the ethylene fragment is considered to be only weakly perturbed in structure and normal modes of vibration from the ethylene molecule. The structure is taken to be that of a planar ethylene fragment with the loosely bound H atom located on an axis perpendicular to the ethylene plane and through one carbon atom. The ethylene fragment is assumed to have regular trigonal bond angles and C-H bond lengths of $1.08\text{ \AA}$. The $\text{C}\cdots\text{H}$ reaction coordinate is assumed to have a bond order of 0.02. Conservation of bond order requires the $\text{C}\cdots\text{C}$ bond to have a bond order of 1.98. Bond lengths of the partial bonds are calculated from Pauling's rule¹⁹ with single bond lengths for C - C and C - H of 1.536 and $1.08\text{ \AA}$, respectively. This results in a $\text{C}\cdots\text{C}$ bond length of $1.358\text{ \AA}$ and a $\text{C}\cdots\text{H}$ bond length of $2.10\text{ \AA}$. Vibration frequencies for the complex are

essentially the experimental values of the ethylene molecule¹⁵ with the addition of two low valued bending frequencies for the reaction coordinate and a revision of the C...C stretching frequency to 1615 cm^{-1} . The latter frequency is slightly lower than the corresponding frequency for ethylene in accordance with Pauling's and Badger's rules.¹⁹ The frequencies of the two bending modes of the rupturing C...H bond are assumed to be degenerate and represent the only adjustable parameter in all of the theoretical calculations. A frequency assignment of 120 cm^{-1} gives the best overall agreement between the calculated and experimental fall-off behavior for this system. These frequencies are also artificially grouped to aid in the economical numerical computation of the sum of vibrational states and are also given in Table I.

Case IV: The geometric structures of C_2D_5 and $\text{C}_2\text{D}_4\cdots\text{D}^\ddagger$ are exactly the same as those assigned to the completely protonated models. Frequency assignments for C_2D_5 are obtained by application of the group frequency method to the observed fundamentals for C_2D_4 and C_2D_6 . All frequency assignments for C_2D_5 are derived in exactly the same way as those for C_2H_5 , with the exception of three degrees of freedom: the $\text{D}_2\text{C-CD}_3$ stretching frequency, the frequency for internal rotation about the C-C bond, and the out-of-plane bending frequency associated with the sp^2 -hybridized carbon. The stretching frequency is determined by treating the radical as a pseudo-diatomic molecule with the force constant reported by Purnell and Quinn.¹⁷ In order to apply the product rule to all of the internal degrees of freedom of the radicals, C_2D_5 and C_2H_5 , the frequency ratio for internal rotation must be specified. The approximate ratio for rotational frequencies may be obtained²⁰ as

$$\nu_R/\nu_R' \approx \left(I'/I \right)^{1/2} \quad (6)$$

where I represents, in this case, the reduced moment of inertia for the free internal rotation, and the primed quantities refer to the deuterated radical. The out-of-plane bending frequency for the methylene group of C_2H_5 (485 cm^{-1}) is used and the corresponding frequency for C_2D_5 is left as the unknown to be determined by application of the Teller-Redlich product rule.

The detailed frequency model for $C_2D_4 \cdots D^\ddagger$ is determined in the same way as the model for $C_2H_4 \cdots H^\ddagger$. Vibration frequencies are assigned to the normal modes of the ethylene fragment which are essentially the fundamentals of C_2D_4 .¹⁵ This leaves three internal degrees of freedom yet to be determined: the frequencies of the two bending modes of the $C \cdots D$ reaction coordinate, which are assumed to be degenerate, and the frequency of the decomposition mode, or reaction coordinate. Although the reaction coordinate, $\nu_L^\ddagger$, is a non-genuine vibration and there is no way to determine the absolute value of this "frequency", the ratio of "frequencies" of the reaction coordinate for isotopically substituted species may be approximated by,²¹

$$\frac{\nu_L^\ddagger}{\nu_L^{\ddagger'}} \approx \left[\left(\frac{1}{M_\alpha} + \frac{1}{M_\beta} \right) / \left(\frac{1}{M_\alpha'} + \frac{1}{M_\beta'} \right) \right]^{1/2}, \quad (7)$$

where M_α and M_β are the masses of the two fragments of the decomposition and the primed quantities refer to the isotopically substituted species.

The frequency of the degenerate bending mode of the reaction coordinate is then determined, relative to that for the protonated case, by application of the product rule. The resulting models for C_2D_5 and $C_2D_4 \cdots D^\ddagger$ are thus designed to be consistent with the models of the light ethyl radical and complex and are given in Table I.

Case II: In addition to the model for the ethyl- d_1 radical and the model for the complex which describes the decomposition of $C_2H_4D^*$ back to initial reactants, $C_2H_4 \cdots D^\ddagger$, an additional model must also be specified to describe the decomposition of $C_2H_4D^*$ by H-atom dissociation, $C_2H_3D \cdots H^\ddagger$. The methods employed to specify these models are analogous to those used for the completely protonated and completely deuterated cases. However, for normal modes of each of the three models which have partial C-H and partial C-D character, the group frequency is calculated as a weighted geometric mean frequency with the appropriately weighted mean frequencies of C_2H_4 , C_2D_4 , C_2H_6 , and C_2D_6 .²² For example, the ethyl- d_1 radical possesses 5 stretches with a mean frequency of 2819 cm^{-1} . This is a weighted mean of 2 C-H stretches of $-CH_3$ character at 2961 cm^{-1} , 2 C-H stretches of $-CH_2$ character at 3047 cm^{-1} , and 1 C-D stretch of $-CD_3$ character at 2185 cm^{-1} . The three remaining internal degrees of freedom for each model of this system are determined as discussed above for Case IV. Here again, consistency between models for the mixed isotope version, $D + C_2H_4$, and the $H + C_2H_4$ system is insured with the product rule. Therefore the models for C_2H_4D , $C_2H_4 \cdots D^\ddagger$, and $C_2H_3D \cdots H^\ddagger$ are designed to be consistent with the models of the light ethyl radical and complex and are given in Table I.

Case III: Model specification for C_2D_4H , $C_2D_4 \cdots H^\ddagger$, and $C_2D_3H \cdots D^\ddagger$ is carried out in exactly the same way as described for case II. These models are also given in Table I.

The thermochemistry of the reactions must also be established in order to apply the theory. For case I, the critical energy is defined by the enthalpy of reaction for ethyl decomposition by H atom rupture plus the energy of activation for the bimolecular addition step, each evaluated at 0°K. In agreement with MS, $E_{OH} = \Delta H_O + E_{AO} = 37.3 + 2.7 = 40.0 \text{ kcal mole}^{-1}$ for the completely protonated case. In order to maintain consistency between each of the deuterated cases and the completely protonated case, critical energies for the deuterated versions are calculated from E_{OH} of case I. If the potential energy difference between the surface describing the ethyl radical and the surface describing the activated complex is defined as V, then the following relationships hold:

$$V = E_{OH} - E_z^\ddagger + E_z \quad (8A)$$

$$V' = E_{oi}' - E_{zi}'^\ddagger + E_z', \quad (8B)$$

where E_z and $E_z^\ddagger$ are the zero-point vibrational energies of the radical and complex, respectively, and the primed quantities in (8B) refer to any particular decomposition mode for the isotopically substituted systems. Since the potential energy surfaces for the protonated and deuterated cases are identical, or nearly so, (8A) may be equated with (8B) with the result

$$E_{oi} = E_{OH} + \Delta E_z - \Delta E_z^\ddagger \quad (9)$$

where Δ refers to the energy for the protonated case less the energy for the deuterated case. The zero-point energies are obtained from the specified molecular models. The critical energies for the four ethyl radical systems are listed in Table I. All of these values are based on the critical energy of 40.0 kcal mole⁻¹ for decomposition of C₂H₅.

The reaction path degeneracy factor ρ_i for each particular decomposition mode i must also be calculated. In the completely protonated case, free internal rotation of the active ethyl radical permits any of the three C-H bonds of the methyl group to rupture from either side of the two-fold symmetric methylene group. Therefore, there are six possible paths for dissociation. The same is true for case IV. This agrees with the more formal interpretation of path degeneracy by the group theoretical treatment of Schlag²³ and also the statistical factor method of Laidler.²⁴ Path degeneracy factors for the mixed isotope cases are calculated in the same way. These factors are also listed in Table I.

The F factor is generally applied to the overall adiabatic rotations to account for centrifugal energy changes during the conversion of an energized molecule to an activated complex.²⁵ This factor may be calculated on the basis of the rigid rotor diatomic approximation given by Marcus.²⁶ For loose activated complexes leading to dissociation, the rotational energies of the energized molecule and complex, E_J and $E_J^\ddagger$, respectively, differ primarily for two rotations in which the two resulting decomposition fragments are treated as the "atoms" of a diatomic molecule.

However, application of the Marcus approximation to the decomposition of ethyl radicals is not entirely straightforward since the rotations about the axis of the pseudo-diatomic, i.e., $C_2H_4 \cdots H$, are not coincidental with the adiabatic rotations of the radical and complex. Fortunately, for the present systems, the motion that occurs upon transformation of the radical to the complex is that of a relatively low mass H or D atom. Therefore, there is little change in the moments of inertia and hence little change in centrifugal energy. Consequently, centrifugal energy effects in the present study are negligible and the F factor is considered to be unity in these calculations.

The strong collision assumption is used in these calculations even though helium is generally considered to be a weak collider,²⁷ i.e., activated species are still able to undergo decomposition despite one or more collisions with the bath gas. The occurrence of inefficient collisions is accounted for by a collision efficiency factor β_{He} . Relative collisional deactivation efficiencies (β_M) for various diluent gases have been derived from chemical activation data for $C_2H_5^*$.⁵ The Lennard-Jones corrected collision efficiency for SF_6 as the diluent gas is assumed to be unity. The multiplicative factor, $\beta_{He} = 0.25$, brings the data for helium into coincidence with the SF_6 data on a collisional basis. Hence β_{He} represents the Lennard-Jones corrected efficiency factor for the strong collisional case. This efficiency factor is assumed to be constant and, for the sake of simplicity and consistency, the same value is used for all four chemical activation systems of the present study.

Results and Discussion

The specific rate constant for decomposition of an activated ethyl radical is given by

$$k_E = \frac{\ell \sum_{E^\ddagger_{vr} = 0}^{E^\ddagger} P(E^\ddagger_{vr})}{h N^*(E = E_0 + E^\ddagger_{vr})} \quad (10)$$

where E refers to a particular level of activation $\geq E_0$. Due to thermal energy contributions from the reactants, the ethyl radicals are formed with a distribution of energies and the distribution function is given by Eq. (11),

$$f(E)dE = \frac{k_E K(E)dE}{\int_{E_0}^{\infty} k_E K(E)dE} \quad (11)$$

where $K(E)dE$ is the Boltzmann distribution for excited ethyl radicals at the temperature of interest. For each of the four ethyl radical systems, k_E and E_0 in Eq. (11) refer to the decomposition mode which results in reformation of the initial reactants, that is: k'_{ED} and E'_{OD} for case II, and k''_{EH} and E''_{OH} for case III. The average energy spread of the ethyl radicals formed at 23°C by chemical activation is only a few kcal mole⁻¹. The full width at half maximum of the distribution function for cases I, II, III, and IV is 2.2, 2.2, 2.5, and 2.6 kcal mole⁻¹, respectively. The distribution functions of activated ethyl radicals tend to broaden slightly with increasing D substitution due to small differences in heat capacities and thermal energies of the species. In each case, an average value of the rate constant for decomposition may be obtained by evaluation of k_{Ei} over the appropriate

distribution function. In case I, for example, $\langle k_{EH} \rangle = \int_{E_{OH}}^{\infty} k_{EH} f(E) dE$.

Average values of the specific rate constants for decomposition in each of the other three cases are calculated in the same way for a temperature of 23°C. Other quantities of interest include the average excess energy of the radicals $\langle E \rangle$, and complexes $\langle E_1^\ddagger \rangle$, each evaluated with respect to their own zero of energy. The results of these calculations are summarized in Table II.

For the completely protonated case, E_{OH} ($= 40.0 \text{ kcal mole}^{-1}$) is the critical energy for H-rupture and it is also the minimum excess energy, E_{min} , for decomposition of the formed ethyl- d_0 radicals with respect to their own zero of energy. Also, since $E = E_0 + E^\ddagger$, the minimum excess energy of $C_2H_5^*$ with respect to C - H rupture is $E_{H min}^\ddagger = 0$ since the decomposition channel is the reverse of the activation process. The same is true for the ethyl- d_5 radical, for which $E_{OD}'' = E_{min}'' = 41.5 \text{ kcal mole}^{-1}$. The difference in critical energy for these two cases, calculated with Eq. (9), results mainly from the difference in C - H and C - D bond energies.

In the mixed isotope cases, $C_2H_4D^*$ and $C_2D_4H^*$ may decompose by either C - H or C - D bond rupture and $E_{min}^\ddagger$ is not necessarily zero. Figure 1 shows the relationships between k'_{EH} , k'_{ED} , and $f'(E)$ as functions of the active energy E' of the chemically activated ethyl- d_1 radical. Since $C_2H_4D^*$ is formed by D atom addition to C_2H_4 , both k'_{ED} and $f'(E)$ originate at E'_{min} , which is equal to E'_{OD} ($= 41.82 \text{ kcal mole}^{-1}$). However, mainly because of the difference in C - H and C - D zero-point energies, the critical energy for H rupture is $E'_{OH} = 39.95 \text{ kcal mole}^{-1}$. Therefore $E_{D min}^\ddagger = 0$ but $E_{H min}^\ddagger = 1.87 \text{ kcal mole}^{-1}$. Hence for any given excitation energy $E' \geq E'_{OD}$, decomposition of $C_2H_4D^*$ by H-rupture is favored both statistically (by a factor of $\rho_H/\rho_D = 2$) and energetically (by $E_{H min}^\ddagger - E_{D min}^\ddagger = 1.87 \text{ kcal mole}^{-1}$)

over decomposition by D-rupture. At 23°C the average excess energies of $C_2H_4D^*$, $C_2H_4 \cdots D^\ddagger$, and $C_2H_3D \cdots H^\ddagger$ are 43.74, 1.92, and 3.79 kcal mole⁻¹, respectively.

The effects of a change in temperature may also be seen with reference to Figure 1. An increase in temperature would increase E' , broaden $f'(E)$, and cause a decrease in the ratio $E_H^\ddagger/E_D^\ddagger$, which would tend to decrease the magnitude of the intramolecular kinetic isotope effect k'_{EH}/k'_{ED} . Conversely, a decrease in temperature would result in an increased magnitude in the isotope effect. In either case, however, a normal kinetic isotope effect is predicted.

The $H + C_2D_4$ system is quite different. Figure 2 shows the relationships between k''_{EH} , k''_{ED} , and $f''(E)$ as functions of the active energy E'' of the chemically activated ethyl- d_4 radical. In this system $C_2D_4H^*$ is formed by H atom addition to C_2D_4 , hence k''_{EH} and $f''(E)$ originate at $E''_{min} = E''_{OH} = 39.76$ kcal mole⁻¹. Since $E''_{OD} = 41.35$ kcal mole⁻¹, a significant fraction of the formed ethyl- d_4 radicals do not possess enough excess energy to undergo D-rupture. For this case, $\ell_H/\ell_D = 1/2$ and for any given energy $E'' \geq E''_{OH}$ of the $C_2D_4H^*$ radical, $E_H^\ddagger = E_D^\ddagger + 1.59$ kcal mole⁻¹. Hence decomposition of $C_2D_4H^*$ by D-rupture is favored on statistical grounds, but decomposition by H-rupture is favored on energetic grounds. At 23°C the average excess energies of $C_2D_4H^*$, $C_2D_4 \cdots H^\ddagger$, and $C_2D_3H \cdots D^\ddagger$ are 41.79, 2.03, and 0.44 kcal mole⁻¹, respectively. Reference to Figure 2 shows that at lower temperatures, where $f''(E)$ becomes closer to a δ function, decomposition of $C_2D_4H^*$ by D-rupture would not be possible. However, at elevated temperatures, corresponding to excess energies of $C_2D_4H^*$ which are greater than 52 kcal mole⁻¹, decomposition of the ethyl- d_4 radical by D-rupture should become the dominant channel for dissociation. At higher temperatures the difference in energetics becomes less important and the statistical factor ℓ_H/ℓ_D begins to dominate the intramolecular isotope effect.

The parameter assignments given in Table I are used to evaluate each of the integral quantities in equations (2)-(5). However, in order to calculate the absolute magnitude of the apparent bimolecular rate constant for each case, the value of the rate constant for the activation step must be known (k_1 for case I, etc.). In case I, for example, inspection of Eq. (2) shows that k_1 is the high pressure limit of the apparent bimolecular rate constant, k_{app} .

$$\text{As } \omega \rightarrow \infty, k_{app} \rightarrow k_1 \int_{E_{OH}}^{\infty} f(E) dE = k_1 \quad (12)$$

Experimental values for k_1 are available in the literature;^{1-6,10,28} however, even the most recently reported values range from 9×10^{-13} ²⁸ to 16×10^{-13} ⁶ cc molecule⁻¹ sec⁻¹. The value for k_1 reported by Eyre, et al.,²⁸ (9×10^{-13} cc molecule⁻¹ sec⁻¹) was obtained with H₂ as the bath gas over a pressure range of 750-1750 torr. Other reported values involved the application of extrapolation techniques to non-linear plots of apparent rate constants which were measured at pressures below the high pressure limit. The accepted value for k_1 in this study is 11.1×10^{-13} cc molecule⁻¹ sec⁻¹ and is within the range of the recently reported values.

Based upon the model parameters in Table I and the accepted value for k_1 , the calculated absolute fall-off behavior of k_{app} for the H + C₂H₄ reaction is shown as the solid curve in Fig. 3 (case I). This is a plot of k_{app} as a function of $\log_{10} (\beta \omega)$, where β is unity for the theoretical calculations. In order to compare the calculated fall-off curve with the behavior of the experimental rate constants, the experimental pressures of the deactivating third body species are converted, as before,⁶ to the

appropriate collision frequencies with the kinetic theory of gases. Also, since helium is less efficient in collisional energy transfer than larger polyatomic molecules, the collision efficiency factor $\rho_{\text{He}} = 0.25$ is included in the conversion of experimental pressures to effective collision frequencies.

For comparison, the resultant calculated fall-off curve and the experimental data for the completely protonated case are shown in Fig. 4, case I. The experimental rate constants in this figure cover an extended pressure range of 0.3 to 600 torr He and 0.25 to 2.93 torr SF_6 , and represent room temperature chemical activation data from five different sources.^{3,5,7,10} It can be seen that the fit of the calculated fall-off curve to the experimental data is excellent over the entire pressure range.

Similar to the fully protonated case, the rate constant for the activation step in each of the deuterated cases is equivalent to the high pressure limit of the apparent bimolecular rate constant (see equations 3-5). Unfortunately, values for k_1' , k_1'' , and k_1''' have not been reported. Therefore, to maintain consistency with case I, they are evaluated from isotope effect calculations with Absolute Rate Theory (ART).²¹ With ART, which is appropriate for high pressure bimolecular rate constants, the problems of calculating ratios of rate constants becomes a matter of calculation of ratios of isotopic partition functions. In addition to the model parameters for $\text{C}_2\text{H}_5^\ddagger$, $\text{C}_2\text{H}_4 \cdots \text{D}^\ddagger$, $\text{C}_2\text{D}_4 \cdots \text{H}^\ddagger$, and $\text{C}_2\text{D}_5^\ddagger$, these calculations require the vibration frequencies and moments of inertia for C_2H_4 and C_2D_4 . All parameters for these calculations are summarized in Table I. Therefore, based upon the accepted value for k_1 , the predicted values for cases II, III, and IV are $k_1' = 8.4 \times 10^{-13}$, $k_1'' = 11.8 \times 10^{-13}$, and $k_1''' = 8.7 \times 10^{-13}$, respectively, all in units of $\text{cc molecule}^{-1} \text{ sec}^{-1}$. As an internal consistency check, estimates of the high pressure rate constants have also been made by another

isotope effect ratio technique. Ratios of k_1 to k_1' , k_1'' , and k_1''' have been calculated with Bigeleisen's method²¹ which uses the Teller-Redlich product rule. The results are within a few percent of those estimated by ART.

Comparison between theory and experiment: The rate constants for activation and the model parameters in Table I, all of which are consistent with case I, are used to theoretically predict the absolute magnitude of the apparent bimolecular rate constants for each of the deuterated cases with equations (3) - (5). For the completely deuterated system, case IV in Fig. 4, the theoretically predicted fall-off curve is nearly in quantitative agreement with the experimental data.

The agreement between the predicted fall-off curves and the observed behavior for the mixed isotope cases is shown in Fig. 5. Case II, the $D + C_2H_4$ reaction, results in quantitative agreement between theory and experiment. The open circles are the experimental values of the apparent bimolecular rate constant at helium pressures ranging from 1 to 5 torr, and the solid line is the predicted behavior. The dotted line and solid circles represent the fraction of excited ethyl- d_1 radicals which are removed through decomposition by H atom rupture (D_H'), and the dashed line and solid squares represent the fraction which are removed by collisional stabilization (S'). For this system at low pressure, decomposition of $C_2H_4D^*$ by C-H bond rupture is the completely dominant reaction path and the mechanism essentially reduces to a fast isotope exchange reaction.

For the chemical activation reaction of H with C_2D_4 , case III in Fig. 5, the apparent bimolecular rate constants agree quantitatively with the theoretical prediction, but only semi-quantitative agreement is obtained for the fraction of excited ethyl- d_4 radicals which are removed by stabilization (S^*)

and by decomposition by D atom rupture (D_D''). However, in view of the constraints imposed in these calculations, the agreement is still quite satisfactory. The slight disagreement very likely does not result from any deficiency in the RRKM theory or the molecular models. Instead, the deficiency probably results either from the naive collision model assumed for the calculations or from a breakdown in the Teller-Redlich product rule. The possible deficiency of the assumption of strong collisions with a constant efficiency factor for helium ($\beta_{He} = 0.25$ for all four cases) will be discussed below in terms of other studies of collision energy transfer models for inert bath gases.

The other possibility for disagreement in S'' and D_D'' is a deficiency in the product rule. On the basis of identical force fields for isotopic molecules, the product rule should hold rigorously for the zero-order frequencies, and at least to a good approximation for the observed fundamentals for any mass difference.¹³ However, application of the product rule to the reported fundamentals¹⁵ of C_2H_4 and C_2D_4 , and to the fundamentals¹³ of C_2H_6 and C_2D_6 results in disagreements of 8% and 36%, respectively. If the frequency assignments of the complexes for case III are appropriately adjusted, quantitative agreement between theory and experiment for k''_{app} , S'' , and D_D'' may be obtained, within experimental error. The fit is accomplished by artificially adjusting the stretching frequencies of the H- and D-rupture complexes in a way which reduces the difference in critical energies to $0.8 \text{ kcal mole}^{-1}$ as calculated with Eq. (9). The resulting product rule agreement between $C_2H_5^+$ and the adjusted models of $C_2D_4 \dots H^+$, and $C_2D_3H \dots D^+$ is 11.5% and 12.5%, respectively. Even though the product rule agreement is less than 13%, this method involves the application of additional adjustable

parameters and is therefore outside the theme of the present study.

Theoretical analysis of fall-off behavior and nonequilibrium kinetic isotope effects: The calculated fall-off curves for all four cases in Fig. 3 show the variations in magnitude and pressure-dependence of the apparent bimolecular rate constants. As discussed above, the fall-off curve for case I is the result of a fit to the experimental data, while the curves for the three isotopically substituted cases are theoretical predictions. On comparison of the fall-off behavior of the apparent bimolecular rate constants for cases I - IV in figures 3, 4, and 5, several features become apparent. Most striking is the fact that the value of k'_{app} for the $D + C_2H_4$ system is virtually insensitive to changes in pressure, whereas the apparent rate constants for all of the other cases show a marked pressure fall-off behavior. Another feature is that the apparent rate constant for the $H + C_2H_4$ reaction is greater than that of the $D + C_2D_4$ reaction at high pressures ($\omega > 10^9 \text{ sec}^{-1}$), but less at lower pressures ($\omega < 10^8 \text{ sec}^{-1}$). Therefore a normal kinetic isotope effect is calculated at high pressures, $k_{app}/k''_{app} > 1$, but this crosses over to an inverse isotope effect at low pressures.

Comparison of case I and case IV in Fig. 4 shows that the mechanism for reactant depletion is exactly the same in the two cases. The apparent rate constant k_{app} (or k''_{app}) at a particular pressure is a measure of the fraction of excited ethyl radicals which are removed by collisional stabilization, S (or S''), where

$$S = \int_{E_{OH}}^{\infty} \frac{\omega f(E)}{k_{EH} + \omega} dE \quad (13)$$

and the apparent rate constant may be given in terms of stabilization as $k_{app} = k_1 S$. In the limit of high pressure as $\omega \rightarrow \infty$, $S \rightarrow 1$ and $k_{app}/k_{app}''' \rightarrow k_1/k_1''' = 1.276$, and a normal isotope effect is predicted. In the low pressure limit, $\omega \approx \omega''' \rightarrow 0$ and both k_{app} and k_{app}''' approach zero; however, according to equations (2) and (5), the isotope effect can be given as ω , $\omega''' \rightarrow 0$ by

$$\left(\frac{k_{app}}{k_{app}'''} \right)_0 \longrightarrow \frac{\omega k_1 \int_{E_{OH}}^{\infty} \frac{f(E)}{k_{EH}} dE}{\omega''' k_1''' \int_{E_{OD}}^{\infty} \frac{f'''(E)}{k_{ED}} dE} \approx \frac{k_1 \langle k_{EH}^{-1} \rangle}{k_1''' \langle k_{ED}^{-1} \rangle} = 0.113 \quad (14)$$

The reason for this crossover to an inverse isotope effect at lower pressures may be understood in terms of equation (10) which, after rearrangement and some cancellation, becomes

$$k_{EH}^{-1}/k_{ED}'''^{-1} = \frac{N_H^*(E)}{N_D^{*''}(E)} \frac{\sum P_D'''(E_D^\ddagger)}{\sum P_H(E_H^\ddagger)} \quad (15)$$

Since the F factor of equation (10) is considered to be unity in all of these calculations, equation (15) should properly include the ratios of partition functions for the adiabatic rotations. However, the ratio of rotational partition functions is very close to unity in all of these systems and will therefore be neglected.

Therefore the ratio of specific rate constants for decomposition is controlled by the sum and density ratios. For the two cases under consideration, ethyl- d_0 and ethyl- d_5 , the average excess energies for each species are listed in Table II. The average excess energies of the complexes differ by only $0.2 \text{ kcal mole}^{-1}$ and the excess energies of the radicals differ by $1.7 \text{ kcal mole}^{-1}$, with the deuterated species being at a higher total energy mainly because of the difference in C-H and C-D bond energies. Since the vibrational energy level spacing, $h\nu$, decreases with substitution of D for H, both $\sum P(E)$ and $N^*(E)$ increase with increasing numbers of substituted D atoms in the radical and complex. However, the ratio of sums $\sum P_D'' / \sum P_H$ generally increases to a lesser degree than the ratio of densities $N_D^{*''} / N_H^*$, at low energies.⁸ These effects are known as statistical-weight isotope effects, since they arise from changes in the numbers of quantum states at various energy levels (the statistical weights of these levels). Thus, in equation (15), the activated complex sum ratio, $\sum P_D^{*''} / \sum P_H$, is greater than unity, but the radical density ratio $N_H^* / N_D^{*''}$ is much less than unity. The radical density ratio dominates the expression because the activated complex energy is at a relatively low level, $E^\ddagger = E - E_0$, while the radical energy is E . Hence a large normal quantum statistical-weight isotope effect is predicted for the $k_{EH} / k_{ED}^{*''}$ ratio, and this appears as a large inverse isotope effect in the low pressure region of the rate constant ratio $k_{app} / k_{app}^{*''}$.

At high pressures ($\omega > 10^9 \text{ sec}^{-1}$), where most of the $C_2H_5^*$ and $C_2D_5^*$ radicals are removed by collisional stabilization, the isotope effect is due primarily to $k_1 / k_1^{*''}$. At lower pressures ($\omega < 10^8 \text{ sec}^{-1}$)

decomposition begins to dominate over stabilization for removal of the excited radicals. Since $C_2D_5^*$ is longer lived than $C_2H_5^*$, the ethyl- d_5 radical has a greater probability of becoming stabilized by collisional energy transfer; hence $S''' > S$ for a particular collision frequency and the isotope effect k_{app}/k_{app}'' is due primarily to k_{EH}^{-1}/k_{ED}^{-1} .

Returning now to the $D + C_2H_4$ system, the insensitivity of k'_{app} to changes in pressure (figures 3 and 5) may be explained in terms of equation (3). Reference to this equation shows that in the limit of zero pressure, as $\omega' \rightarrow 0$,

$$k'_{app} \rightarrow k'_1 \int_{E'_{OD}}^{\infty} \frac{k'_{EH} f'(E)}{k'_{EH} + k'_{ED}} dE = k'_1 \left\langle \frac{k'_{EH}}{k'_{EH} + k'_{ED}} \right\rangle, \quad (16)$$

where the bracketed average-value-term is calculated to be 0.91. Therefore, even in the limit of zero pressure, the apparent bimolecular rate constant is already 91 percent of the way to its high pressure limiting value of k'_1 . The reason for this is that decomposition of the chemically activated ethyl- d_1 radical by H-rupture is the dominant channel for dissociation. The energetics for this system are given in Table II and the relationship between k'_{EH} , k'_{ED} , and $f'(E)$ as functions of the energy E' of the $C_2H_4D^*$ radical are shown in Fig. 1. Equation (10) may be applied in this case to gain insight into the intramolecular isotope effect. Since both H- and D-rupture occur from the same excited ethyl- d_1 radical, the density terms $N^{*'}(E)$ in equation (10) for either decomposition mode are identical and the isotope effect is given by

$$\frac{k'_{EH}}{k'_{ED}} = \frac{\ell'_H}{\ell'_D} \frac{\sum P'_H(E_H^\ddagger)}{\sum P'_D(E_D^\ddagger)} \quad (17)$$

According to the result obtained from Eq. (16), decomposition of $C_2H_4D^*$ by D-rupture only accounts for 9% of the total decomposition events. This leads to an intramolecular kinetic isotope effect of $k'_{EH}/k'_{ED} = 10.1$. As discussed above, decomposition of $C_2H_4D^*$ by H-rupture is favored statistically and energetically over decomposition by D-rupture. The dominant effect in the rate ratio of equation (17) for this case is the difference in critical energies $E'_{oD} - E'_{oH} = 1.87 \text{ kcal mole}^{-1}$, which causes $E_H^\ddagger$ to be greater than $E_D^\ddagger$. For any given energy E' ($\geq E'_{oD}$) of $C_2H_4D^*$, $\sum P'_D(E_D^\ddagger)$ is evaluated at $E_D^\ddagger = E' - E'_{oD}$ and $\sum P'_H(E_H^\ddagger)$ is evaluated at $E_H^\ddagger = E_D^\ddagger + 1.87 \text{ kcal mole}^{-1}$. Hence both the sum ratio and reaction path degeneracy ratio in equation (17) are greater than unity and contribute to a large normal kinetic isotope effect. The reaction path degeneracy ratio, ℓ'_H/ℓ'_D , contributes a factor of 2 to the isotope effect while the sum ratio contributes a factor of 5. Hence the non-equilibrium, intramolecular kinetic isotope effect for decomposition of chemically activated ethyl- d_1 radicals (formed by D atom addition to C_2H_4 at 296°K) is 5.0 per rupturable atom.

Reference to figures 3 and 5 shows that a very slight fall-off of the rate constant is predicted for effective collision frequencies of $(1-5) \times 10^8 \text{ sec}^{-1}$; for this range of pressure, since $\langle k'_{EH} \rangle \approx 2.7 \times 10^8 \text{ sec}^{-1}$, stabilization (S') of $C_2H_4D^*$ competes with decomposition by H-rupture (D'_H). For $\omega' < 10^8 \text{ sec}^{-1}$, k'_{app} is independent of pressure and D'_H is the dominant channel for removal of $C_2H_4D^*$; for $\omega' > 5 \times 10^8 \text{ sec}^{-1}$, S' becomes the dominant channel for removal of $C_2H_4D^*$ and k'_{app} again becomes pressure-independent (see case II in Fig. 5).

Although the $\text{H} + \text{C}_2\text{D}_4$ reaction is mechanistically similar to the $\text{D} + \text{C}_2\text{H}_4$ reaction, reference to Fig. 5 shows that the ethyl- d_4 system behaves quite differently. Unlike the fall-off behavior of the ethyl- d_1 system, the fall-off behavior of k''_{app} for case III more closely resembles that of the ethyl- d_0 and ethyl- d_5 cases (see Fig. 3). The apparent bimolecular rate constant for the $\text{H} + \text{C}_2\text{D}_4$ system is given by Eq. (4); in the limit of zero pressure as $\omega'' \rightarrow 0$,

$$k''_{\text{app}} \rightarrow k''_1 \int_{E''_{\text{OH}}}^{\infty} \frac{k''_{\text{ED}} f''(E)}{k''_{\text{EH}} + k''_{\text{ED}}} dE = k''_1 \left\langle \frac{k''_{\text{ED}}}{k''_{\text{EH}} + k''_{\text{ED}}} \right\rangle \quad (18)$$

where the value of the term in brackets for this case is 0.13. Hence in the low pressure limit k''_{app} is only 13% of the way to its high pressure limiting value of k''_1 . Unlike the ethyl- d_1 system, decomposition of $\text{C}_2\text{D}_4\text{H}^*$ by the path which results in depletion of reactant ethylene (H-rupture in case II and D-rupture in case III) is not the dominant dissociation process. According to the result obtained from Eq. (18), decomposition of $\text{C}_2\text{D}_4\text{H}^*$ by D atom rupture accounts for 13% of the total decomposition events and this results in an intramolecular kinetic isotope effect of $k''_{\text{EH}}/k''_{\text{ED}} = 6.7$. The magnitude of this ratio may also be interpreted with Eq. (17), where each quantity is represented by double primes for this case. As discussed above with reference to Fig. 2, decomposition of $\text{C}_2\text{D}_4\text{H}^*$ by D-rupture is favored statistically but decomposition by H-rupture is favored energetically. Because of the difference in critical energy, $E''_{\text{CD}} - E''_{\text{OH}}$, $\sum P''_{\text{H}}$ is evaluated at $E''_{\text{H}} = E''_{\text{D}} + 1.59 \text{ kcal mole}^{-1}$ while $\sum P''_{\text{D}}$ is evaluated at E''_{D} for any energy

$E'' (\geq E''_{OH})$; furthermore, for values of $E'' \leq E''_{OD}$, the value of $\sum P''_D$ is unity. These factors cause the sum ratio of equation (17) to be greater than unity and contribute to a large normal isotope effect which is partially compensated by the reaction path degeneracy ratio. The path degeneracy ratio, ℓ_H/ℓ_D , contributes a factor of 0.5 to the isotope effect given by Eq. (17) while the sum ratio contributes a factor of 13.4. Hence, the nonequilibrium, intramolecular kinetic isotope effect for decomposition of chemically activated ethyl- d_4 radicals (formed by H atom addition to C_2D_4 at $296^\circ K$) is 13.4 per rupturable atom.

Comparison of the magnitude of the intramolecular isotope effect per rupturable bond (5.0 for case II and 13.4 for case III) shows that the isotope effect is much larger for case III, ethyl- d_4 decomposition. The difference in magnitude is due primarily to the difference in C-H and C-D bond energies. Reference to Fig. 1 shows that all of the ethyl- d_1 radicals formed by D atom addition to C_2H_4 possess sufficient energy to undergo C-D bond rupture. However, reference to Fig. 2 shows that C-D bond rupture is energetically not allowed for a major fraction of the ethyl- d_4 radicals formed by H atom addition to C_2D_4 . For energies of $C_2D_4H^*$ between 39.76 and 41.35 kcal mole $^{-1}$, only H-rupture can occur from $C_2D_4H^*$.

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Table I. Parameter Assignments
(*indicates active rotations)

Species	Vibrational frequencies (cm ⁻¹) frequency (degeneracy)	Moments of inertia (gm cm ² molecule ⁻¹ x 10 ⁴⁰)				Critical energy of reaction (kcal mole ⁻¹)	Reaction path degeneracy
		I _A	I _B	I _C	I _{red}		
C ₂ H ₅	2995 (5)	40.21	37.28	8.40*	1.89*		
	1428 (4)						
	1025 (2)						
	974 (2)						
	485 (1)						
C ₂ H ₅ [‡]	3047 (4)	36.21	35.11	12.81*	--	40.00	6
	1463 (3)						
	1001 (2)						
	972 (3)						
	120 (2)						
C ₂ D ₅	2220 (5)	57.68	51.83	16.78*	3.81*		
	1074 (4)						
	862 (2)						
	764 (2)						
	311 (1)						
C ₂ D ₅ [‡]	2274 (4)	53.60	52.19	24.84*	--	41.50	6
	1168 (3)						
	766 (2)						
	742 (3)						
	84 (2)						
C ₂ H ₄ D	2819 (5)	42.94	40.30	10.04*	2.08*		
	1332 (4)						
	1017 (2)						
	898 (2)						
	477 (1)						

Table I. (Cont.)

Species	Vibrational frequencies (cm ⁻¹) frequency (degeneracy)	Moments of inertia (gm·cm ² molecule ⁻¹ × 10 ⁴⁰)				Critical energy of reaction (kcal mole ⁻¹)	Reaction path degeneracy
		I _A	I _B	I _C	I _{red}		
C ₂ H ₄ ...D [‡]	3047 (4)	43.54	36.79	18.46*	--	41.82	2
	1455 (3)						
	1001 (2)						
	972 (3)						
	101 (2)						
C ₂ H ₃ D...H [‡]	2832 (4)	39.04	38.47	14.08*	--	39.95	4
	1383 (3)						
	936 (2)						
	909 (3)						
	117 (2)						
C ₂ D ₄ H	2360 (5)	54.89	48.85	14.80*	3.56*		
	1152 (4)						
	868 (2)						
	828 (2)						
	338 (1)						
C ₂ D ₄ ...H [‡]	2274 (4)	50.89	46.17	18.69*	--	39.76	2
	1170 (3)						
	766 (2)						
	742 (3)						
	105 (2)						
C ₂ D ₃ H...D [‡]	2447 (4)	51.40	48.34	23.01*	--	41.35	4
	1230 (3)						
	819 (2)						
	793 (3)						
	89 (2)						

Table I. (Cont.)

Species	Vibrational frequencies (cm ⁻¹) frequency (degeneracy)	Moments of inertia (gm cm ² molecule ⁻¹ x 10 ⁴⁰)				Critical energy of reaction (kcal mole ⁻¹)	Reaction path degeneracy
		I _A	I _B	I _C	I _{red}		
C ₂ H ₄	3047 (4)	33.85	28.09	5.76			
	1623 (1)						
	1392 (2)						
	1027 (1)						
	1001 (2)						
	946 (2)						
C ₂ D ₄	2274 (4)	49.41	37.90	11.51			
	1515 (1)						
	1028 (2)						
	726 (1)						
	766 (2)						
	749 (2)						

Table II. Theoretical Results

System	$\langle E \rangle^a$	$\langle E_i^\ddagger \rangle^a$	$\langle k_{Ei} \rangle \text{ sec}^{-1}$
I. $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5^*$	41.92		
$\text{C}_2\text{H}_5^* \rightarrow \text{C}_2\text{H}_4 + \text{H}$		1.92	1.76×10^8
II. $\text{D} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{D}^*$	43.74		
$\text{C}_2\text{H}_4\text{D}^* \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}$		3.79	2.72×10^8
$\text{C}_2\text{H}_4\text{D}^* \rightarrow \text{C}_2\text{H}_4 + \text{D}$		1.92	3.74×10^7
III. $\text{H} + \text{C}_2\text{D}_4 \rightarrow \text{C}_2\text{D}_4\text{H}^*$	41.79		
$\text{C}_2\text{D}_4\text{H}^* \rightarrow \text{C}_2\text{D}_4 + \text{H}$		2.03	1.44×10^7
$\text{C}_2\text{D}_4\text{H}^* \rightarrow \text{C}_2\text{D}_3\text{H} + \text{D}$		0.44	7.72×10^6
IV. $\text{D} + \text{C}_2\text{D}_4 \rightarrow \text{C}_2\text{D}_5^*$	43.66		
$\text{C}_2\text{D}_5^* \rightarrow \text{C}_2\text{D}_4 + \text{D}$		2.16	2.81×10^7

^aAverage energies are given in units of kcal mole⁻¹.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

(b). Application of the RRKM Theory of Unimolecular Reactions to the
H + C₂H₂/He, H + C₂D₂/He, D + C₂H₂/He, D + C₂D₂/He
Chemical Activation Systems

Introduction

The application of RRKM theory of unimolecular reactions to the decomposition of vibrationally excited ethyl radicals successfully explains the pressure dependence of apparent bimolecular rate constants for the chemical activation system H + C₂H₄/He and its isotopic variations^{1,2,3,4}. The determination of the pressure dependence of the apparent bimolecular rate constants for the chemical activation system H + C₂H₂/He and its isotopic variations^{2,3} required that an effort be made to further test the predictive ability of RRKM theory for the decomposition of vinyl radicals. Thus a consistent theoretical model has been developed for the structure and vibrational frequencies of the protonated and isotopically substituted vinyl radicals and activated complexes. Since the unimolecular rate constants obtained from the theoretical treatment can only be related to the bimolecular rate constants through the relation³

$$k_{bi}/k_1 = k_{uni}/k_{uni}^{\infty} \quad (1)$$

it was also necessary to obtain estimates for the high pressure limit to the bimolecular rate constants, k_1 , in those cases where the experimental measurement had not been made. These estimates were obtained through absolute reaction rate theory calculations that were consistent with the specified model and the known experimental data on activation energies. Finally the

relative collisional deactivating efficiency of third body species with vinyl radicals and the critical energy for decomposition of vinyl radicals were estimated.

MODEL SPECIFICATION AND ABSOLUTE REACTION RATE THEORY CALCULATIONS

Since the experimental data on the pressure dependence of the reaction $H + C_2H_2/He$ was available over a much larger pressure range (0.5 to 742 torr^{2,3,5}) than any of the other systems, our efforts centered on developing a model that could successfully predict its pressure dependence. Several estimates of the value of k_1 , the high pressure limiting bimolecular rate constant were available: extrapolation of data obtained from a time resolved Lyman α photometric system³ in this laboratory indicated $k_1 = 2.18 \pm 0.33 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, whereas the extrapolation of data over a smaller pressure range from a fast flow-system coupled to ESR and a mass spectrometer⁵ indicated $k_1 = 1.18 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Information about the high pressure limiting rate constants for the isotopic variations was limited to the experimental observation that k_{app} for the reaction $D + C_2H_2$ was very nearly pressure independent. This observation was made with the discharge flow TOFMS system in this laboratory² over the pressure range 1 to 5 torr and by others⁶ in a fast flow-ESR, mass spectrometric system over the range 1 to 15 torr. These observations coupled with the knowledge that in the ethylene system $D + C_2H_4$ is very near its high pressure limit even at low pressure⁴ indicate that k_1 for $D + C_2H_2$ may be² $\sim 1.22 \times 10^{-13} \text{ cc molecule}^{-1} \text{ sec}^{-1}$; an additional piece of information⁶ for this system is that $k_1 = 5.15 \times 10^{-11} \exp\left(\frac{-3700 \pm 200 \text{ cal mole}^{-1}}{RT}\right) \text{ cc molecule}^{-1} \text{ sec}^{-1}$.

With these initial criteria in mind theoretical models were constructed for the vinyl radical and activated complex; the geometry of the radical and complex are shown in Fig. I and the moments of inertia and vibrational frequencies are listed in Table I. The details of determining the vibrational frequencies

for the vinyl radical are similar to the methods used for the ethyl radical^{1,2,3,4} and will not be listed here. The activated complex for the vinyl system was designated as a "loose complex" and as a result all of the vibrational frequencies are identical to acetylene except the low frequency bending vibration which was left as an adjustable parameter.

Absolute reaction rate theory calculations for the reaction $D + C_2H_2 \rightleftharpoons C_2H_2 \cdots D^\ddagger \rightarrow C_2H_2D$ (I) with these model activated complexes involves the following expression:

$$k_1 = \frac{\kappa \ell kT}{h} \frac{Q_T^\ddagger Q_R^\ddagger}{Q_T^A Q_T^M Q_R^M} \left\{ \frac{\prod_{i=1}^7 (1 - \exp(-\nu_i^M/kT))}{8 \prod_{i=1}^8 (1 - \exp(-\nu_i^\ddagger/kT))} \right\} \exp(-E/RT) \quad (2)$$

where it is assumed that κ , the transmission coefficient, is unity; ℓ , the reaction path degeneracy is 2; $Q_T^\ddagger$, Q_T^A , Q_T^M are the translational partition functions of the complex, reactant atom and reactant molecule respectively; $Q_R^\ddagger$, Q_R^M are rotational partition functions; $\nu_i^\ddagger$, ν_i^M are the vibrational frequencies of the complex and reactant molecule; E is the energy difference from the zero point energy of the reactant molecules to the zero point energy of the activated complex. The model parameters specified in Table I and the assumptions made above leave k_1 and E as the only unspecified quantities in equation (2).

The assumption that this reaction is already at its high pressure limit $k_1 = 1.22 \times 10^{-13}$ cc molecule⁻¹ sec⁻¹ yields $k_1 = 2.82 \times 10^{-10} \exp(-\frac{4590 \text{ cal mole}^{-1}}{RT})$ cc molecule⁻¹ sec⁻¹ which is in reasonable agreement with the value quoted earlier. Acceptance of this value for E determines E for all

of the isotopically substituted systems since

$$E = E_B + E_Z^\ddagger - E_Z^M \quad (3)$$

where $E_Z^\ddagger$, E_Z^M are the zero point energies of the activated complex and reactant molecule. As a result the calculation from the reaction

yields $k_1 = 4.09 \times 10^{-10} \exp \left(\frac{4617 \text{ cal mole}^{-1}}{RT} \right) \text{ cc molecule}^{-1} \text{ sec}^{-1}$. At 298°K $k_1 = 1.68 \times 10^{-13} \text{ cc molecule}^{-1} \text{ sec}^{-1}$, and this value falls between the two estimates extrapolated from the available experimental data.

RRKM CALCULATIONS

In order to do a complete calculation, information about the relative collisional deactivating efficiency of third body species and vinyl radicals as well as the critical energy of reaction of vinyl radicals was required. Results from a time resolved Lyman α photometric system in this laboratory¹ indicate that the relative efficiencies of He and SF₆ are approximately equal: $\beta_{He} = \beta_{SF_6} = 1$. The estimation of the critical energy for decomposition of vinyl radicals requires ΔH for the reaction of decomposition of the radical and the activation energy for the reverse process of radical formation. The activation energies were estimated from the model as described above. The ΔH for decomposition of vinyl radicals is uncertain because of uncertainties in the heat of formation of vinyl radicals.^{7,8,9} An estimate⁹ of $\Delta H_{298}^0 = 69$ was tentatively accepted and the critical energies listed in Table I were calculated. Complete RRKM calculations were performed on the completely protonated case only and the result is compared to the experimental values

in Figure 2. The computational procedures are exactly analogous to those employed in ethyl radical calculations^{1,2,3,4} and are omitted here.

RESULTS AND DISCUSSION

The theoretical predictions based on this model show reasonable agreement with the experimental data in the fall off region but consistently indicate lower values of k_{app} in the low pressure regime. The theoretical quantity plotted is

$$k_{bi} = k_1 (k_{uni}/k_{uni}^\infty) = k_1 \int_{\epsilon_0}^{\infty} \frac{\omega f(\epsilon) d\epsilon}{\omega + k_\epsilon} \quad (4)$$

when ω is the collision frequency of excited radicals with third body species,

$$f(\epsilon) = \frac{\int_0^{\epsilon^\ddagger} P(\epsilon_{vr}^\ddagger) \exp(-\epsilon^\ddagger/RT) d\epsilon^\ddagger}{\int_0^{\infty} \sum_{\epsilon^\ddagger} P(\epsilon_{vr}^\ddagger) \exp(-\epsilon^\ddagger/RT) d\epsilon^\ddagger} \quad (5)$$

and

$$k_\epsilon = \frac{\ell}{h} \frac{\sum_{\epsilon^\ddagger} P(\epsilon_{vr}^\ddagger)}{N^*(\epsilon) \cdot F} \quad (6)$$

The adjustable parameter in the model is the low frequency bending vibration in the activated complex and adjustment of this parameter serves only to shift the fall off region by changing $\sum_{\epsilon^\ddagger} P(\epsilon_{vr}^\ddagger)$ in k_ϵ . Other changes of model parameters that affect $\sum_{\epsilon^\ddagger} P(\epsilon_{vr}^\ddagger)$ and/or $N^*(\epsilon)$ do not appreciably improve the fit between theory and experiment. Thus no changes are indicated in the basic model. The fit to the experimental data does depend on the initially calculated parameter k_1 . The uncertainty in this quantity represents a major obstacle

to further theoretical work on this system. Consequently the time dependent Lyman α photometric apparatus has been modified so that k_1 for $H + C_2H_2/He$ can be measured. The details of this modification and some preliminary investigations with the new system are reported in Section B of this report.

References

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Table I. Parameter Assignments

Species	Vibrational Frequencies		Moments of Inertia			Critical Energy of Reaction (kcal/mole)	Reaction Path Degeneracy
	frequency (cm ⁻¹)	degeneracy	(g. cm ² molecule ⁻¹ x 10 ⁴⁰)				
			A	B	C		
C ₂ H ₃	3330	(1)	2.93	26.56	29.49		
	1760	(1)					
	1383	(1)					
	3004	(1)					
	818	(1)					
	1001	(1)					
	3090	(1)					
	760	(1)					
	946	(1)					
-155- C ₂ H ₃ [‡]	100	(1)	4.29	25.54	29.83	41.517	2
	612	(2)					
	729	(2)					
	1974	(1)					
	3330	(2)					
C ₂ H ₂ D	3330	(1)	4.28	29.26	33.54		
	1739	(1)					
	1192	(1)					
	2586	(1)					
	765	(1)					
	876	(1)					
	2680	(1)					
	759	(1)					
	842	(1)					
C ₂ H ₂ →D [‡]	3330	(2)	8.40	26.82	35.22	42.813	1
	1974	(1)					
	612	(2)					
	729	(2)					
	81	(1)					

Table I (cont)

Species	Vibrational Frequencies		Moments of Inertia			Critical Energy of Reaction (kcal/mole)	Reaction Path Degeneracy
	frequency (cm ⁻¹)	degeneracy	(g. cm ² molecule ⁻¹ x 10 ⁴⁰)				
			A	B	C		
CHCD...H [‡]	2935	(2)	4.31	30.52	34.83	41.132	1
	1851	(1)					
	519	(2)					
	683	(2)					
	96	(1)					
C ₂ D ₂ H	2560	(1)	9.05	33.89	42.95		
	1698	(1)					
	1192	(1)					
	2586	(1)					
	676	(1)					
	876	(1)					
	2680	(1)					
	595	(1)					
842	(1)						
CDCH...D [‡]	2935	(2)	8.69	31.20	39.89	42.169	1
	1851	(1)					
	519	(2)					
	683	(2)					
	77	(1)					
C ₂ D ₂ ...H [‡]	2560	(2)	4.34	34.92	39.26	40.545	1
	1762	(1)					
	505	(2)					
	539	(2)					
	96	(1)					

Table I (cont)

Species	Vibrational Frequencies		Moments of Inertia			Critical Energy of Reaction (kcal/mole)	Reaction Path Degeneracy
	frequency (cm ⁻¹)	degeneracy	(g. cm ² molecule ⁻¹ x 10 ⁴⁰)				
			A	B	C		
C ₂ D ₃	2560	(1)	5.85	36.34	42.19		
	1672	(1)					
	1028	(1)					
	2225	(1)					
	632	(1)					
	766	(1)					
	2324	(1)					
	594	(1)					
	749	(1)					
-157- C ₂ D ₃ [‡]	2560	(2)	8.61	35.95	44.56	41.671	2
	1762	(1)					
	505	(2)					
	539	(2)					
	76	(1)					

Vinyl Radical

Activated Complex

Fig. 2