ELEMENTARY RATE CONSTANTS FOR HYDROGEN ATOMS

1972-73

ANNUAL PROGRESS REPORT

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1972-1973

I. GENERAL REPORT

A. INTRODUCTION

This Annual Progress Report summarizes work done under Contract AT(11-1)-3242 (formerly AT(30-1)-3794) for the year 1972-1973. This is the seventh complete year for this contract. During this period the contract has supported the research of eleven workers including the principal investigator. Five of these workers have successfully defended Ph.D. theses which have been submitted to the Department of Chemistry at Carnegie-Mellon University. They are Drs. J. R. Barker, D. T. Osborne, C. T. Yeh, G. N. Suess, and D. G. Keil. All of these students are actively pursuing careers as professional scientists. It is a pleasure to report that two more students will be submitting Ph.D. theses in the near future based on work carried out under this contract. They are J. J. Ahumada and T. C. Schwab.

In past years this contract has supported the construction of and experimentation with six experimental apparatuses. This has included tuition and salary support of students. The principal purpose of the experimentation has been to develop techniques to measure the absolute rate constants for hydrogen atoms with various substrate reactions in the gas phase. The work to date has concentrated on the pressure dependence of various reactions at room temperature only. However, temperature dependence studies are now underway. This new work allows for the complete description for elementary rate constants of these atom-molecule reactions.

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 the report.

B. PERSONNEL

The principal investigator on this project is Associate Professor Joe V. Michael of Carnegie-Mellon University. The Contract has supported thesis research of seven graduate students during the past year. These are:

Mr. David G. Keil; B.A., Thiel College, 1967

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

Mr. Gregory N. Suess; B.A., Franklin and Marshall College, 1967

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

Mr. Jorge J. Ahumada; B.S., Universidad Nacional de Colombia, 1962

Mr. Kevin P. Lynch; B.S., Mt. St. Mary College, 1968

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

Two of these have terminated their work on completion of all Ph.D. degree requirements. They are Drs. G. N. Suess and D. G. Keil. Mr. S. D. Gleditsch, who recently joined the research group as a first-year graduate student will also terminate on submission of a thesis for the M.S. degree. He plans to pursue a career in medicine. It is a pleasure to report that Mr. K. P. Lynch, a first-year graduate student, has joined the group and has expressed a desire to submit a Ph.D. thesis to the department based on work done under this Contract.

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.

Some permanent equipment was purchased during the sixth contract year.

This equipment is:

A Raytheon PGM-10X-1 Microwave Power Generator

D. MANUSCRIPTS SUBMITTED FOR PUBLICATION

Absolute Quenching Cross Sections of $\text{Hg}(^3\text{P}_1)$ with Various Molecules,

J. V. Michael and G. N. Suess.

The Chemical Kinetic Effects of Walls on Active Species: Results for Hydrogen Atoms, J. J. Ahumada and J. V. Michael.

E. 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 $H + C_2H_4$: 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 $Hg(^3P_1) + H_2$ and the Imprisonment Lifetimes for $Hg(^3P_1)$ at Low Opacity, J. V. Michael and C. Yeh, J. Chem. Phys. 53, 59 (1970).

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

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

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

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

F. MANUSCRIPTS IN PREPARATION

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

Further $Hg(^3P_1)$ Quenching Studies, S. D. Gleditsch and J. V. Michael

$H + C_2H_4$: Deuterium Variations and RRKM Calculations, J. A. Cowfer, D. G. Keil, and J. V. Michael.

G. THESES

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

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

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

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

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

H. ACKNOWLEDGEMENTS

The principal investigator and graduate students whose research has been supported completely by the Atomic Energy Commission under Contract AT(11-1)-3242 wish to gratefully acknowledge this support. We also want to thank the administrative officers of Carnegie-Mellon University for their capable handling of clerical details associated with this contract. We also acknowledge the cooperation and support of the Chemistry Department at Carnegie-Mellon University under the Chairmanship of Professor Albert A. Caretto, Jr., 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

Introduction

This apparatus has not been used during the current contract period. However, the technique which has been described in conjunction with it has been used on a modified reactor which is attached to the time-of-flight mass spectrometer (Experiment E). During the current contract period several absorption calibrations of various photometer configurations have been carried out. This work was suggested in last year's renewal proposal and has now been completed. The cross checking which is possible with combined analysis of H atom concentrations (Lyman- α photometry from the work of J. R. Barker^{1,2} and that of D. G. Keil² with the time-of-flight mass spectrometer) allows a test of internal consistency within this laboratory and also fixes the operation of new photometer configurations.

Experimental

The apparatus has been described in conjunction with Experiment E in the 1967-68 Annual Progress Report.² The principal modification was the inclusion of two side arms normal to the flow in the reactor section which served as the path length for Lyman- α photometry. LiF blanks were sealed onto these side arms and various photometer configurations were tested. The measured absorption path was 7.0 cm. Quantitative analysis could be performed with the TOF mass spectrometer from a measure of the H₂ peak height before and after turning on the microwave discharge. We have used this procedure for several years and know it to be accurate from NO₂ titration calibrations.

Results and Discussion

The procedure to obtain the amount of light other than Lyman- α was to flood the system with atoms. Two detectors were tested (NO ionization detector and

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EMR model 542G-09-18 photomultiplier tube). If the amount of light which was not Lyman- α is subtracted from both $I_{\text{O}\alpha}$ and I_{α} the results for both detectors are identical within the error of the determination. The first photometer configuration which was tested is that reported by J. R. Barker^{1,2} from this laboratory. In this previous work the absorption path length was 2.4 cm as compared to the 7.0 cm. value here. The Lyman- α lamps are essentially identical in all respects, i.e., they are 6.7 cm in length and are neon filled static lamps operating at 60 cycles A.C. at identical voltages. The amount of light which is not Lyman- α was determined to be 15% of the total intensity. This has been confirmed in these new experiments. The smooth curve from the Beer's law (T vs. $[H]$) of Barker is replotted as T vs. $N\ell$ simply by multiplying $[H]$ by 2.4 cm. Similarly the present results on T vs. $[H]$ (where $[H]$ is determined from mass spectrometric determination) is plotted as T vs. $N\ell$ where $\ell = 7.0$ cm. If the analyses are correct $(N\ell)_{\text{JRB}}$ vs. $(N\ell)_{\text{TOF}}$ should be a straight line with unit slope. This correlation is very good as can be seen in Figure I where this comparison between J. R. Barker's results and the time-of-flight results is presented. The slope of the line is 1.09 ± 0.2 . These results then confirm Barker's results independently.

A second photometer system was calibrated. This is the type used by D.T. Osborne and J. J. Ahumada² in this laboratory. The neon filled static lamp is driven by a 28.8 MHz Hartley oscillator. It has been found that the amount of light other than Lyman- α is larger for this configuration and depends on the photodetector. The atom flooding experiments indicate 36.2% for the NO ionization detector and 42% for the photomultiplier detector. The corrected transmittances as a function of $N\ell$ are however identical within experimental error as seen in Table 1. Inspection of Table 1 and comparison with the data of Barker shows the present configuration to be about four times less sensitive for atom detection. This fact has been used by J. J. Ahumada and G. N. Suess to assess absolute atom concentrations in earlier results obtained in Experiment B.

for any kind of thing to know, and it is (about half a century ago) that we have seen the first appearance of the first of the great works of the great men of the world.

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Relative photometer operation has been carried out with the techniques of Experiment B. This apparatus associated with Experiment B has been rebuilt (see Experiment B for details). The Lyman- α lamp is of a design originally described by Davis and Braun.³ It is a counterflow He (2 torr) discharge which is microwave driven (no added H_2 and operated at 15% power). The detector is a Bendix M-306 electromultiplier or EMR solar blind photomultiplier. In these experiments a NO ionization detector was also used. The atoms were formed photochemically at 100 torr H_2 by mercury photosensitization and the steady state transmittances were observed as a function of relative mercury light intensity. Intensity was varied by screens of various transmittances. Four photometer configurations were checked and two of these have been described in connection with the absolute TOF experiments, namely the radio frequency driven static lamp with NO ionization detector and EMR phototube. The other two configurations are the Davis and Braun lamp with the two modes of detection mentioned above. The data was collected for these four configurations and the only quantity necessary to calculate transmittances was the amount of extra light for each configuration. The fractions were known for the RF driven configuration from the absolute calibration (TOF) but no estimates could be made for the Davis-Braun Lyman- α lamp because steady state concentrations were not high enough with this apparatus to flood the photometer. Instead the same photometer was used with the shock tube apparatus (Experiment D) and H_2 was shocked at temperatures in excess of 3000°K. The fraction of extra light determined in this fashion for the Davis-Braun lamp with EMR photomultiplier was $14 \pm 2\%$. Since the band pass for the NO detector is much smaller than that of the phototube (see absolute data above for extra light) the fraction for this configuration is assumed to be 0%. The corrected transmittances can then be calculated for the four configurations and these are given in Table II. The worst signal to noise in the configurations of Table II is for the radio frequency-nitric oxide detector

configuration. These results are good to $\pm 2\%$. It is clear that equivalence of results is independent of the type of detection which is used if the extra light fractions are known. Also it is apparent that the behavior of the Davis-Braun lamp is within $\pm 1\%$ in transmittance to the radio frequency lamp. Since an absolute calibration (T vs. $N\ell$) is known for the radio frequency lamp, this same calibration can be used for the Davis-Braun configuration. As stated previously the radio frequency configuration is four times less sensitive (for the same ℓ) as that used by Barker and the same can now be said for the Davis-Braun configuration. The question arises as to whether this operation is consistent with the known oscillator strength of $H(^2P_{3/2,1/2}) \leftarrow H(^2S_{1/2})$.

Line Absorption Calculation for the Davis-Braun Lamp

Braun, Bass and Davis⁴ have suggested a two absorption layer model for characterizing emission-line profiles of a counterflow electrodeless microwave discharge lamp similar to that used in this experiment. The model requires that a finite concentration of absorbing species exists between the discharge zone and the window of the lamp. The lamp design of this experiment satisfies this requirement as a result of low pumping-speed and, therefore, an increased probability of back diffusion of absorbing species from the discharge zone exists. Therefore, the two absorption layer model has been adopted and the method of Ladenburg and Reiche⁵ has been chosen to develop an expression for the absorbance of resonance lines. The expression is as follows:

$$A = 1 - \frac{\sum_i \int_{-\infty}^{+\infty} C_i \exp \left\{ -(\omega_i/\alpha_i)^2 - \ell \sum_j k_{oj} \exp(-\omega_j^2) - \ell_r \sum_j k_{rj} \exp \left[-(\omega_j/\beta_j)^2 \right] \right\} d\omega_i}{\sum_i \int_{-\infty}^{+\infty} C_i \exp \left\{ -(\omega_i/\alpha_i)^2 - \ell_r \sum_j k_{rj} \exp \left[-(\omega_j/\beta_j)^2 \right] \right\} d\omega_i}, \quad (1)$$

where C_i is proportional to the statistical weight of the upper level in the i^{th}

transition, k_{oj} , is the absorpton coefficient at the center of the j^{th} line and α_i is the ratio of discharge temperature to the absorber temperature.

$$\alpha_i = \left(\frac{T_e}{T_a} \right)^{\frac{1}{2}} \quad (2)$$

Doppler reversal due to thermal atoms present in the dead space in the lamp is considered in the parameters k_{rj} , ℓ_r , and β_j where k_{rj} is the absorption coefficient at the center of the j^{th} line for the absorbing layer within the source, ℓ_r is the thickness of the absorbing layer within the source and β_j is defined as the ratio of the Doppler width of the reversal absorbing line within the source to that of the external absorbing line and may be written,

$$\beta_j = \left(\frac{T_r}{T_a} \right)^{\frac{1}{2}}, \quad (3)$$

where T_r is the gas temperature in the absorbing layer within the lamp and T_a is the absorber temperature.

Equation (1) contains the parameters α_i , β_j , and $k_{rj} \ell_r$ as well as the variable $k_{oj} \ell$. The complexity of the calculation is reduced by defining values for α_i and β_j ($\alpha_i = 1.3$, $\beta_j = 1.05$) from experimental measurements (glass-covered thermocouples). Other assumptions employed were that $\beta_1 = \beta_2 = \beta$, $\alpha_1 = \alpha_2 = \alpha$, $k_{o2} = 2k_{o1}$, $k_{r2} = 2k_{r1}$, and $C_2 = 2C_1$.

All calculations were performed with a CDC G-20 electronic computer. The integrals in Equation (1) were evaluated numerically and values of absorbances were calculated as a function of $k_{o1} \ell$ and $k_{r1} \ell_1$.

An optimum value of the parameter $k_{r1} \ell_1$ may be found, the criterion being that a linear relationship must exist between $k_{o1} \ell$ and $N\ell$. This restriction is imposed by the definition of the oscillator strength were the oscillator strength for atomic transition, f_1 , is related to k_{o1} by the expression,

$$P_1 = \left(\frac{1}{2}\right) (\Delta v_D) (\pi / \ln 2)^{\frac{1}{2}} (mc / \pi e^2) \left(\frac{k_{o1}}{N}\right), \quad (4)$$

$$k_{o1} = \frac{2}{\Delta v_D} \frac{\sqrt{\ln 2}}{\pi} \frac{\lambda_o^2}{8\pi} NA_{21} = 1.143 \times 10^{-13} \text{ cm}^2 \text{ N},$$

where Δv_D is the Doppler width of the absorption line, m is the electron mass, e is the electronic charge, $\lambda_o = 1215.607 \text{ \AA}$, A_{21} is the Einstein transition probability, and N is the number of atoms per cubic centimeter in the absorption cell.

The results obtained from Equation (1) have been interpreted with the criteria that α and β are fixed and that k_{o1} varies only with concentration. If $k_{r1} \ell_r$ is assumed to be zero (no absorption in the lamp), the plot of $k_{o1} \ell$ vs. $N \ell$ gives a curve with negative deviation from a straight line in disagreement with Equation (4). This implies that either the $\alpha = 1.3$ value is too small (i.e., if α is 1.7 straight line behavior is obtained) or finite atom concentrations which absorb within the lamp exist (i.e., $k_{r1} \ell_r \neq 0$). The value of α of 1.7 implies $T_e = 897^\circ \text{K}$, a value which is totally unreasonable. Furthermore the f value predicted from the $\alpha = 1.7$ fit is only 15% of the theoretical value of 0.1387 for the weakest line. Again this behavior is unreasonable. Thus, it is concluded that $k_{r1} \ell_r$ must be nonzero. The results of this analysis have shown that the required straight line behavior of $k_{o1} \ell$ vs. $N \ell$ is obtained for the values of $k_{r1} \ell_r = 1.8-2.2$. The value of $k_{r1} \ell_r = 2.0$ gives the best overall fit and results of $k_{o1} \ell$ vs. $N \ell$ correlation for the data of Tables I and II is shown in Figure II. The best straight line gives a slope of $1.0 \times 10^{-13} \text{ cm}^2$. Use of Equation (4) implies an oscillator strength of 0.121 for the weakest line. This is better than to be expected agreement with the theoretical value of 0.1387.

The question arises as to whether the value of $k_{r1} \ell_r = 2.0$ is a reasonable result. k_{r1} may be calculated similarly to k_{o1} (Equation (4) except Δv_D must be

replaced by Δv_{Dr}) and the result is $k_{r_1} = 1.035 \times 10^{13} \text{ cm}^2 \text{Nr}$. The measured value of ℓ_r is 7.0 cm which gives $k_{r_1} \ell_r = 7.6 \times 10^{13} \text{ cm}^3 \text{Nr}$. If $k_{r_1} \ell_r$ is to be 2.0 this implies a value of $\text{Nr} = 2.6 \times 10^{12} \text{ atoms/cm}^3$. The question now becomes whether this value of concentration is reasonable from discharged liquid N_2 cooled tank He with no added H_2 . The grade of He is C.D. grade. This is the same purity He used in this laboratory by J. R. Barker^{1,2} in his experiments several years ago. It was never possible to completely remove attenuation of Lyman- α from "pure" tank He on discharging the flow even by liquid N_2 cooling. Measured transmittance varied between 90% and 95% even with cooling for the first photometer configuration which was considered in this part of the report. This would indicate that an atom concentration of $\sim .8\text{--}1.5 \times 10^{12} \text{ atoms/cc}$ is possible from "pure" tank He. Dissociation is complete under these conditions and this would indicate an H_2 impurity level in the He of ~ 30 parts per million. The stated impurity level of C.D. grade He is 50 parts per million. All of the considerations lead us to conclude that $k_{r_1} \ell_r = 2.0$ is possible and the correspondence with the known oscillator strength adds further confidence to the line absorption calculation.

With this model the line shape can be calculated and the results will agree well with the conclusions of the calculations of Braun, Bass, and Davis.⁴ We propose, then, to use this line shape to extract photometer behavior of absorbing atoms at temperatures up to 3000°K and, therefore, the absorption data which we have already obtained for the shock tube experiment (Experiment D) can be reported in terms of absolute rates of H atom production. This will then allow absolute rate constants to be determined for this apparatus.

References

1. J. V. Michael, et al. 1966-67 Annual Progress Report AEC-NYO-3794-1.
2. J. V. Michael, et al. 1967-68 Annual Progress Report AEC-NYO-3794-3.
3. D. Davis and W. Braun, Appl. Opt. 7, 2071 (1968).
4. W. Braun, A. Bass, and D. Davis, J. Opt. Soc. Am. 60, 166 (1970).
5. A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited States
(Cambridge University Press, Cambridge, England, 1961).

Fig. 1

Table I

T_{α} (a,c)	$N\ell \times 10^{-12}$ (a,d)
0.89	2.9
0.86	4.2
0.84	5.6
0.82	6.4
0.80	11.0
0.76	12.0
0.72	13.0
0.48	27.0
0.44	39.0
0.43	36.0
0.38	44.0
0.37	52.0

T_{α} (b,c)	$N\ell \times 10^{-12}$ (b,d)
0.84	2.4
0.82	2.8
0.79	6.3
0.72	7.7
0.70	9.1
0.52	29.0
0.46	36.0
0.44	40.0
0.43	44.0

- a) Data obtained with radio frequency oscillator lamp and NO detector.
- b) Data obtained with radio frequency oscillator lamp and E.M.R. photomultiplier.
- c) Transmittance values corrected for non-Lyman- α light.
- d) Error of [H] ranges from $\pm 30\%$ at high transmittance to $\pm 15\%$ at low transmittances.

Table II

Mercury Light Filters	T_{α}	T_{α}	T_{α}	T_{α}
	Radio Frequency Oscillator (NO)	Radio Frequency Oscillator (Photo)	Microwave Lamp (NO)	Microwave Lamp (Photo)
0	0.70	0.68	0.69	0.68
5	0.71	0.72	0.72	0.70
1	0.76	0.77	0.78	0.75
2	0.90	0.85	0.85	0.83
3	0.90	0.89	0.91	0.90
4	0.78	0.82	0.84	0.82

Experiment B: Time Resolved Detection of Hydrogen Atoms

I. The Chemical Kinetics Effects of Walls on Active Species: Results for H Atoms

Introduction

The role of wall termination was recognized several years ago in the kinetic of branching chain reactions,¹ but it has not often been considered in non-chain studies in both steady state and time resolved experiments. The usual assumption is that uniform and homogeneous concentrations of atomic and radical species are present throughout a contained volume. Even if this condition holds, non-uniformities in concentration can exist due to the coupling of homogeneous first order reaction, diffusion and heterogeneous reaction at the walls. In this section cases where these processes are important are examined and tested. Energy injection is assumed, for the sake of simplicity, to be uniform and a step function of time.

Model.- Taking into account first order homogeneous reaction, diffusion and heterogeneous wall termination, the continuity equation for the active species is given by

$$\frac{\partial n}{\partial t} = D \nabla^2 n - kn + n_0 \quad (I-1)$$

where n is the active species concentration; D = binary diffusion coefficient of n through heat bath molecules; k = first order rate constant for bimolecular reaction and n_0 = rate of production of n from an external source. ∇^2 = Laplacian operator. It can be shown² that if concentrations are observed radially at the center of a finite cylinder and the axial distance is a few times the radius of the cylinder, then the perturbations due to end walls can be neglected; this has justified the adoption of an infinite cylinder with radius a as the model to be used. In cylindrical coordinates equation (I-1) becomes

$$\frac{\partial^2 n}{\partial r^2} + \frac{1}{r} \frac{\partial n}{\partial r} - \frac{kn}{D} + \frac{n_0}{D} = \frac{1}{D} \frac{\partial n}{\partial t} \quad (I-2)$$

Solutions of equation (I-2) can be found if boundary conditions are specified². In the present cases these conditions are: i) n must be finite at the center of the cylinder ($r = 0$); ii) $\frac{\partial n}{\partial r} + hn = 0$, at $r = a$, where $h = \bar{c}\epsilon/4D$, $\bar{c}$ being the average speed of the active species and ϵ is the wall recombination coefficient;¹ iii) $n = 0$ at $t = 0$. Several cases of interest are now considered:

a) $n_0 = \text{constant}$ and $k = 0$. Under these conditions solution of (I-2) leads to

$$n = \frac{n_0 a}{2hD} + \frac{n_0(a^2 - r^2)}{4D} - \frac{2n_0 h}{aD} \sum_{1}^{\infty} e^{-D\alpha_n^2 t} \frac{J_0(\alpha_n r)}{\alpha_n^2 [\alpha_n^2 + h^2] J_0(\alpha_n a)} \quad (\text{I-3})$$

where J_0 are Bessel functions of the first kind of order zero and the choices of α_n are made according to the roots of $\alpha_n J_1(\alpha_n a) = hJ_0(\alpha_n a)$.^{2a} It is seen that as $t \rightarrow \infty$, equation (I-3) becomes

$$n_{\infty} = \frac{n_0 a}{2hD} + \frac{n_0(a^2 - r^2)}{4D} \quad (\text{I-4})$$

at the steady state. This expression predicts a parabolic distribution of n_{∞} which can be quite severe if ϵ is fairly large, especially at high pressures. The radial average of n obtained from equation (I-3) is

$$\bar{n} = \frac{n_0 a}{2hD} + \frac{n_0 a^2}{8D} + \frac{4n_0 h^2}{a^2 D} \sum_{1}^{\infty} e^{-D\alpha_n^2 t} \frac{1}{\alpha_n^4 [\alpha_n^2 + h^2]} \quad (\text{I-5})$$

b) $n_0 = 0$ and $k = 0$; for this case the boundary condition iii) is replaced by equation (I-4) at $t = 0$, the solution being

$$n = \frac{2n_0 h}{aD} \sum_{1}^{\infty} e^{-D\alpha_n^2 t} \frac{J_0(\alpha_n r)}{\alpha_n^2 [\alpha_n^2 + h^2] J_0(\alpha_n a)} \quad (\text{I-6})$$

This expression for the decay from steady state is exactly complementary to the build-up equation (I-3). The radial average is given by

$$\bar{n} = \frac{4n_0 h^2}{a^2 D} \sum_{1}^{\infty} e^{-D\alpha_n^2 t} \frac{1}{\alpha_n^4 [\alpha_n^2 + h^2]} \quad (\text{I-7})$$

c) $n_0 = \text{constant}$ and $k \neq 0$ in the steady state ($\frac{dn}{dt}=0$) the boundary conditions being given by i) and ii). The solution is

$$n_{\infty} = \frac{n_0}{k} \left[1 - \frac{hI_0(qr)}{qI_1(qa) + hI_0(aq)} \right] \quad (I-8)$$

where $q = (k/D)^{\frac{1}{2}}$ and I_0 and I_1 are the modified Bessel functions of the first kind of order zero and one respectively. Comparison of equation (I-8) with equation (I-4) shows that for the same h and D values the presence of reactant considerably depresses the radial distribution relative to that predicted for the no reactant case a).

The radial average concentrations is given by

$$\bar{n}_{\infty} = \frac{n_0}{k} \left[\frac{(q - \frac{2h}{qa})I_1(qa) + hI_0(qa)}{qI_1(qa) + hI_0(qa)} \right] \quad (I-9)$$

d) $n_0 = 0$ and $k \neq 0$ with boundary condition iii) being replaced by equation (I-8) for $t = 0$. The solution is then

$$n = \frac{2n_0 h}{a} \sum_{n=1}^{\infty} e^{-(D\alpha_n^2 + k)t} \frac{J_0(\alpha_n r)}{[\alpha_n^2 + k][\alpha_n^2 + n^2] J_0(\alpha_n a)} \quad (I-10)$$

with radial average given by

$$\bar{n} = \frac{4n_0 h^2}{a^2} \sum_{n=1}^{\infty} e^{-(D\alpha_n^2 + k)t} \frac{1}{\alpha_n^2 [D\alpha_n^2 + k][\alpha_n^2 + h^2]} \quad (I-11)$$

Comparison of this case with case b) (no reactant) shows that the time exponent has changed by k and also that the amplitude factor is decreased by k in the denominator. The choices of α_n for cases b) and d) are the same as given for case a). Also in all infinite summations, α_1 is the only important root, and thus only one term needs to be retained. As a result of this fact several important points are immediately evident.

- 1) The build-up constant predicted by equation (I-5) will be $D\alpha_1^2$
- 2) The decay constant predicted with the equation (I-7) will be $D\alpha_1^2$.

- 3) The decay constant predicted by equation (I-11) will be $D\alpha_1^2 + k$, so that the effect of homogeneous first order reaction can be separated from diffusion and reaction at the wall from real time experiments with and without reactant.
- 4) The results are independent of radial distribution, an assumption which has been made by many authors in atomic and radical reaction studies.³⁻⁶
- 5) Under conditions of non-reactive or highly poisoned walls (ϵ and h very small), diffusion is no longer important since α_1^2 approaches $\frac{2h}{a} = \frac{\bar{c}\epsilon}{2a}$ for small ϵ and is zero when ϵ is zero, i.e., under these "ideal" conditions the model predicts no decay of active species in the absence of reactants.
- 6) For very large values of ϵ , (h is practically infinity at all values of D) a value of $\alpha_1 a$ of 2.4048^{2a} is predicted, and the time constant for wall destruction will always be $D(2.4048)^2/a^2$, i.e., the removal of active species will be entirely determined by diffusion.
- 7) The model predicts that for experiments in which $\bar{n}_\infty$ is observed as a function of n_o with and without reactant^{7,8} the following expression should hold

$$\frac{[\bar{n}_\infty/n_o]_o}{[\bar{n}_\infty/n_o]_r} = 1 + k\left(\frac{a^2}{8D} + \frac{a}{2hD}\right) = 1 + k\left[\frac{\bar{n}}{n_o}\right]_o \quad (I-12)$$

This equation is identical to equation (8) of reference 7 in which the subscripts o and r refer to the cases with and without reactant respectively.

Experimental

A block diagram of the apparatus used is given in Figure (I-1).

The Lyman- α absorption photometer consists of a 2450 MHz microwave driven flowing He (2 torr) discharge lamp (Raytheon Model PGM-10X-1 with an Evenson cavity from Optos Inst. Co.)^{4,9,10} and a Bendix M306 magnetic electron multiplier which can be operated in steady illumination (electrometer), analog (oscilloscope), or single photon (multichannel analyzer) modes. The present experiments were obtained oscilloscopically. Lyman- α radiation is filtered by 2.2 cm of flowing O_2 at one atmosphere. The windows are one-half inch LiF blanks glued onto the

lamp, cell and photomultiplier assembly with high temperature cement. The lamp is operated with no added H_2 at low microwave power (15-20%). The phototube (RCA 935) located at left of the cell detects the light from the mercury resonance lamp and the resulting pulse serves to trigger a Tektronix 547 oscilloscope or a Nuclear Data 2400 multichannel analyzer. The reaction cell is a 6.7 cm quartz cylinder with inside radius of 1.70 cm. It is surrounded by a ceramic furnace that has a length which is twice the length of the cell. The heating element is nichrome wire and the temperature is measured at various positions outside and inside the cell by means of chromel-alumel thermocouples. No severe axial or radial gradients were found up to $400^\circ C$; temperatures are reported in $^\circ C$ to $\pm 1\%$.

Results and Discussion

Figure (I-2) shows the approach to and decay from steady state of $[H]$ at room temperature at $P_{H_2} = 10$ torr. (This experiment was performed using the apparatus already described in previous reports.^{11,12,13}) The decay constant (k_d) in the dark period is 35.0 sec^{-1} and, according to the model, is equal to $D\alpha_1^2$. Using $D_{H,H_2} = 1900 \text{ cm}^2 \text{ sec}^{-1}/P(\text{torr})$ at $298^\circ K$ ^{14,15} a value for α_1 of 0.445 cm^{-1} is implied, which in turn gives a value for h at 0.208 cm^{-1} ($a = 1.90 \text{ cm}$ for this apparatus) and a value of $\epsilon = 6 \times 10^{-4}$. The calculation of $\frac{\bar{n}}{n_0}$ with these quantities is also shown in Figure (I-2), thus demonstrating the continuous nature of equations (I-5) and (I-7).

Figure (I-3) shows decay constants from reference 3 which were invariant with pressure within 15%; according to this model, this system represents a highly poisoned one with small ϵ ; taking ϵ as 1×10^{-4} the solid line, also shown in this figure, has been calculated.

Decay constants obtained with the apparatus described in the previous section are shown in Table I-1 as a function of total pressure at various temperatures together with calculated values for $D_{H,H_2}\alpha_1^2$ and the values of ϵ used in each

case. Good agreement is obtained between k_d and $D\alpha_1^2$ except at 298°K and 470°K where for pressures above 350 torr no reasonable value of ϵ can predict the observed values of k_d . This may be due to a greater participation of the second order volume termination above 350 torr plus the onset of second order heterogeneous termination processes^{16,17} at the highest temperature; neither of these processes have been considered in the present model. Almost quantitative agreement is obtained at the two lowest temperatures if ϵ is varied downward (two last columns in Table (I-1)), a fact that could be explained if the heat bath molecules acted as surface sites inhibitors. The value of $\epsilon = 1.2 \times 10^{-3}$ used at $T = 298^\circ\text{K}$ is consistent with that reported by Wood and Wise¹⁷ who used a different technique. They obtained 2.8×10^{-3} where the accuracy has been estimated to be $\pm 50\%$. Also, an Arrhenius plot of the ϵ values indicates an activation energy of 2.1 ± 0.2 kcal/mole for the recombination of H atoms on quartz; this result is consistent with a Rideal type mechanism which exhibits a theoretically estimated energy of 2.2 kcal/mole and is predominant from 120 to 500°K.^{16,17} Figure (I-4) shows the variation of k_d with pressure at 369°K. The calculated line, which reproduces the data within experimental error, is obtained with $\epsilon = 2.3 \times 10^{-3}$. Table (I-2) shows the results for H atom decays in Kr at room temperature. The calculated values for $D\alpha_1^2$ are obtained with $\epsilon = 1.0 \times 10^{-3}$ and $D_{H,Kr} = 875 \text{ cm}^2 \text{ sec}^{-1}/P(\text{torr})$. $D_{H,Kr}$ is calculated from the Lennard-Jones parameters for H atoms^{14,15} together with known parameters for Kr.¹⁸

II. Determination of the Dead Time τ in the Single Photon Counting Mode

Introduction

It has been mentioned in the description of the apparatus which was used in Part I of this section that the magnetic electron multiplier can be operated in steady illumination (electrometer), analog (oscilloscope), or single photon (multichannel analyzer) modes. It was found that while transmittances of Lyman- α

which were obtained with the analog and steady illumination modes were the same for a given $[H]_{\infty}$, those obtained in the single photon mode were always higher. This indicated that a correction of the counting rates from the multichannel analyzer was necessary to arrive at the true transmittance. In order to make such a correction, the dead time τ of the detection system (excluding the multiplier) had to be determined. This part summarizes the results of such a determination.

Experimental

Figure (II-1A) shows a block diagram of the detection system which was used to obtain the true and apparent counting rates for a given transmitted light intensity. The photo-current from the multiplier was first measured with a Kiethley 610B electrometer and simultaneously displayed on a potentiometric recorder. The same signal was then fed to the multichannel analyzer via a FET preamplifier, an amplifier, and a pulse height discriminator. Enough counts were accumulated in the multiscale mode to insure good statistics. The output was printed on a Teletype in line with the multichannel analyzer. The light intensity was then varied by moving the lamp away from or closer to the cell and/or with attenuating screens. In this way several pairs of I/k values (where I is the recorded photocurrent and k is a conversion constant) and corresponding R_{obs} (in counts per second) were obtained for each configuration.

It was also found necessary to correct R_{obs} by taking into account an intrinsic recovery time τ' of the multichannel analyzer. In order to determine τ' counting rates were obtained at a given light intensity with different dwell times. The light intensity was then varied and another set of points obtained; this procedure was repeated with a radioisotope (^{22}Na) as the radiation source and a scintillator-photomultiplier arrangement as the detector. The rest of the associated electronic equipment is shown in figure (II-1B).

Results

The determination of τ' was done with a plot of R_{obs} vs. $1/t_d$ (t_d being the dwell time of the multichannel analyzer). τ' was extracted from the value of slope/intercept according to the relation

$$R_{obs}^* = \frac{R_{obs}}{1 - \tau'/t_d} \quad (II-1)$$

An average value for τ' of 2.113 ± 0.005 μ sec was obtained from the results with both arrangements shown in Figure II-1. Figure II-2 shows a typical plot of R_{obs} vs. $1/t_d$.

It is assumed that the true counting rate is $I/k = R$, and the observed counting rate R_{obs}^* are related by¹⁹ (corrected through equation II-1)

$$R_{obs}^* = R e^{-\tau R} \quad (II-2)$$

A plot of $\ln \frac{R_{obs}^*}{I}$ vs. I should then give k as the inverse of the intercept and τ from the values of the slope and intercept. Such a plot is shown in Figure (II-3) from which $k = 2.52 \times 10^{-13}$ coul/count and $\tau = 2.34$ μ sec are obtained. With these values of k and τ , a calculated curve of R_{obs}^* vs. R was obtained and is shown in Figure II-4 together with the experimental points. It can be seen that a relationship of the type given by equation (II-2) is closely obeyed.

For comparison purposes, the value of τ' given by the manufacturer (memory cycle time) is 2.25 μ sec and that of τ determined oscilloscopically in this laboratory for our experimental arrangement is 2.40 μ sec. Also, using the value of k and the charge of the electron, the gain of the Bendix magnetic multiplier is calculated to be 1.57×10^6 in agreement with the manufacturer's specifications under the present operating conditions.

III. New Data for the Reaction $\text{H} + \text{C}_2\text{H}_2$

Introduction

This part contains the results of a study of the reaction $\text{H} + \text{C}_2\text{H}_2$ over a wide pressure range, using He as the diluent gas.

The apparatus and technique employed in this investigation have been described in previous reports.¹¹⁻¹³

Results

Experiments were performed in the pressure range from 6 torr to one atmosphere, and the rate constants are presented in Table III-1 and Figure III-1.

The results seem to indicate that the high pressure limit of k_{app} is not reached until pressures on the order of one atmosphere or greater. At 400 torr the value of k_{app} is already larger than the value for the high pressure limit extrapolated from the data of reference 20, a discrepancy that may be the result of the narrow pressure range studied in reference 20.

A plot of $(k_{\text{app}})^{-1}$ vs. $(P_{\text{T}})^{-\alpha}$ made according to the method of Oref and Rabinovitch²¹ and taken from reference 22 is shown in Figure III-1. In addition to the data of Table III-1, this figure includes those of Keil²² and Osborne.²³ A value of $\alpha = 0.40 \pm 0.05$ was chosen and the intercept for the least-square fit was found to be $(0.0229 \pm 0.0031) \times 10^{14}$ molecule sec cm^{-3} which gives a high pressure limiting rate constant (stoichiometry one) of $(2.18 \pm 0.33) \times 10^{-13}$ cm^3 molecule⁻¹ sec⁻¹.

20. K. Hoyerman, H. Gg. Wagner and J. Wolfrum, Ber. Bunsenges. Phys. Chem., 72, 1004 (1968).
21. I. Oref and B. S. Rabinovitch, J. Phys. Chem., 72, 4488 (1968).
22. D. G. Keil, Ph.D. Thesis, Carnegie-Mellon University (1973).
23. D. T. Osborne, Ph.D. Thesis, Carnegie-Mellon University (1970).

Fig. I-4

Fig. II-1

Fig. II-2

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Fig. II-1. Plot of $(k_{app})^{-1}$ for $H + C_2H_2$ reaction as a function $(P_T)^{-0.4}$.
 ○ - Results of Keil. 22 ◊ - Results of Osborne. 23 ⊗ - New data. Size of the points indicates uncertainties. Solid line is least-squares fit to the data, all points weighted by $(k_{app})^2$. Intercept corresponds to a stoichiometry 2 high pressure limiting rate constant equal to $4.36 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

Table I-1: Decay Constants on Quartz in H₂

T = 298°K				
P(torr)	$k_d(\text{sec}^{-1})$	$D\alpha_1^2(\text{sec}^{-1})^a; \epsilon = 1.2 \times 10^{-3}$	$D\alpha_1^2(\text{sec}^{-1})$	$\epsilon \times 10^3$
700	7.1 ± 0.4	5.2	5.0	0.53
500	8.3 ± 0.7	7.2	6.5	0.53
350	9.6 ± 0.8	10.0	9.0	0.53
200	12 ± 1	16.4	14.0	0.56
100	22 ± 2	28.6	22.5	0.80
50	36 ± 4	44.6	36.0	0.97
10	83 ± 11	78.1	78.1	1.2
1	113 ± 15	87.0	109.5	1.5

T = 333°K				
$\epsilon = 1.8 \times 10^{-3}$				
700	7.5 ± 0.4	6.4	6.2	0.82
500	8.7 ± 0.7	8.9	8.3	0.82
350	12 ± 1	12.5	11.7	0.82
200	17.5 ± 1.5	20.8	19.0	0.94
100	30 ± 3	37.1	31.5	1.1
50	55 ± 6	60.6	54.0	1.4
10	105 ± 15	104.0	104.0	1.8

T = 369°K				
$\epsilon = 2.3 \times 10^{-3}$				
700	8.0 ± 0.4	7.4		
500	11 ± 1	10.3		
350	14 ± 1	14.4		
200	22 ± 2	24.3		
100	40 ± 4	43.0		
50	74 ± 7	74.0		
10	150 ± 30	147.0		

Table I-1 (cont)

T = 420°K

<u>P(torr)</u>	<u>k_d(sec⁻¹)</u>	<u>Dα₁²(sec⁻¹); ε = 3.2 x 10⁻³</u>
700	12 ± 1	9.4
500	13.5 ± 1.0	13.0
350	17.0 ± 1.5	18.2
200	29 ± 3	30.8
100	54 ± 5	56.6
50	90 ± 9	97.5

T = 470°K

ε = 4.5 x 10⁻³

700	21 ± 2	11.3
500	26 ± 2	15.7
350	28 ± 3	22.2
200	44 ± 4	37.2
100	57 ± 6	70.7
50	130 ± 15	125.0

^aThe values for D_{H₂} are taken from refs. 14 and 15: 298°K - 1900/P; 333°K - 2326/P; 369°K - 2675/P; 420°K - 3350/P; and 470°K - 4036/P. D_{H₂} has units of cm² sec⁻¹ and P is in torr.

Table I-2: Decay Constants on Quartz in Kr at 298°K

<u>P</u>	<u>k_d(sec⁻¹)</u>	<u>Dα₁²(sec⁻¹); ε = 1.0 x 10⁻³</u>
700	4.7 ± 0.4	2.4
500	4.5 ± 0.4	3.4
350	6.2 ± 0.6	4.8
250	6.7 ± 0.6	8.0
150	9.7 ± 1.0	10.5
50	19.8 ± 2.0	25.4
10	49 ± 5	55.3

Table III-1

Absolute Rate Constants for the Reaction $\text{H} + \text{C}_2\text{H}_2$ at High Pressures in He Diluent

<u>P_T(torr)</u>	<u>$k_{\text{app}} \times 10^{14} \text{ (cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}\text{)}$</u>
6	4.16 ± 0.55
15	4.82 ± 0.20
25	6.39 ± 0.47
50	6.42 ± 0.42
100	10.14 ± 0.79
200	10.56 ± 0.93
400	16.11 ± 0.92
600	16.88 ± 1.38
742	19.03 ± 0.87

C. Experiment C

Mercury Photosensitized Decomposition of Hydrogen

This experiment was discontinued during the past year, but the apparatus associated with it is still available so that further experiments with it are possible if personnel become interested. The experiment utilizes Lyman- α photometric measurements of H atoms in a steady state photolysis. Quantitative measurements of H atoms have been made as a function of absolute absorbed light intensity,¹ and estimates of the quantum yield of H atom production has resulted. This work has not been published, but the manuscript is in the preparatory stages. It has been necessary to understand the implications of the diffusion to and reaction with the wall problem (see Experiment B, this report) before this manuscript could be completed. Two manuscripts^{2,3} based on this work have been published, however.

References

1. C. T. Yeh, Ph.D. Thesis, Carnegie-Mellon University, 1971.
2. J. V. Michael and C. T. Yeh, J. Chem. Phys. 53, 59 (1970).
3. J. A. Cowfer, D. G. Keil, J. V. Michael, and C. T. Yeh, J. Phys. Chem. 75, 1584 (1971).

D. Experiment D

Shock Tube

Introduction

A direct isothermal measurement has been made of the rate of formation of atomic hydrogen behind shock waves in hydrogen-argon mixtures. The kinetics of this reaction have been studied over a wide range of temperatures, initial pressures and compositions. A rate law has been described which agrees with experimental results. The relative data obtained in this section will be used in conjunction with Section A to obtain absolute rate constants. Comparison of the relative rate constants obtained herein with current experimentation^{1,2} in this system lends credibility to these preliminary results.

Experimental

The apparatus, materials and technique used to obtain the data on $H_2 + M \rightarrow 2H + M$ have been described in the previous report.³ Since this time, two additional pieces of equipment have been added: a Lectronic Research Laboratories Inc. model 111-B crystal calibrator and a Tektronix type 549 storage oscilloscope. The crystal calibrator is used to display accurate time markers on the Polaroid photograph experimental records and the purpose of the oscilloscope is to monitor the flow characteristics of the shock wave. Shock wave flow characteristics (laminar and/or turbulent flow) may be observed from the voltage output of a thin film resistance velocity gauge which represents the temperature profile of the flow. A constant voltage output implies constant wall temperature and, therefore, laminar flow, and a positive deviation from this constant voltage implies an increasing wall temperature or the onset of turbulent flow. This information is necessary for calculating the nonideal shock wave behavior proposed by Mirel's⁴ theory.

There are two principal prerequisites of the technique of atomic resonance absorption spectrophotometry (a.r.a.s.) when applied to shock tube chemical

kinetics. The shock tube and associated high vacuum equipment must be capable of maintaining a very low impurity level (of the order of a few parts per million). Also a well understood resonance line source must be available to provide an appropriately thin line for the absorbing transition of the atoms to be studied. The shock tube in this experiment can be evacuated to a pressure of less than 5×10^{-5} torr with a low enough leak rate that an impurity level of only 5 ppm maximum is developed during the time necessary to complete an experiment. All gases used were obtained commercially from Air Products and Chemicals Inc. Analyses by the supplier's laboratory showed that He (5 ppm) was the major impurity in research grade hydrogen with an oxygen impurity level <1.0 ppm and the major impurity in ultrapure argon was N_2 (5 ppm) with a total impurity level of H_2 and O_2 less than 2 ppm. The description, calibration, and mathematical model describing the resonance line source have been discussed in Section A of this report. The results from this analysis will be used, in conjunction with the relative data presented in this section, to obtain absolute rate constants for H_2 dissociation as a function of temperature and reactant concentration.

Results and Discussion

The rates measured herein are for the dissociation of hydrogen in argon,

through direct observation of the increasing concentration of atomic hydrogen behind a shock wave. Thus for

$$[M] = [M'] + [H_2]$$

$$- \frac{d[H_2]}{dt} = k_d [H_2]^X [M]^Y = \frac{1}{2} \left(\frac{d[H]}{dt} \right). \quad (2)$$

The growth of H-atom concentration is measured by the decrease in transmission of Lyman- α from the resonance light source.³ A first approximation of the relationship between Lyman- α transmittance and H-atom concentration may be made through Beer's law,

$$I = I_0 \exp (-k[H]) \quad (3)$$

which implies

$$- \ln A \propto [H]. \quad (4)$$

The results of the lamp calibration, Section A, may then be used to obtain absolute H-atom concentrations.

As previously stated, the purpose of this experiment was to determine the kinetics of the dissociation of molecular hydrogen highly diluted in argon as a function of temperature and initial pressure and composition. A series of experiments, Table I, were designed to determine the order with respect to argon and hydrogen. Series I, II, and III were used to determine hydrogen order and are presented in Figure I as $\log \frac{dH}{dT}$ vs. $\frac{1}{T}$. The time constants, dH/dT , are represented in relative units as previously discussed.³ The reaction order is then computed from the distance between the parallel lines drawn through each set of points and the following relationship, e.g.

$$\log \left[\frac{(\frac{dH}{dT}) \text{ Series I}}{(\frac{dH}{dT}) \text{ Series II}} \right] = n \log \left[\frac{[H_2] \text{ Series I}}{[H_2] \text{ Series II}} \right] \quad (5)$$

where the left hand side of the equation is the distance between the parallel lines, n is the order with respect to hydrogen and the remaining terms on the right hand side are determined from initial conditions. A similar procedure was used to calculate argon order from series III, IV, and V represented in Figure II. The

relationship used to correlate this data is as follows, e.g.

$$\log \left[\frac{\left(\frac{dH}{dT} \right)_{\text{Series III}}}{\left(\frac{dH}{dT} \right)_{\text{Series IV}}} \right] = n \log \left[\frac{[\text{Ar}]_{\text{Series III}}}{[\text{Ar}]_{\text{Series IV}}} \right] \quad (6)$$

where n is the order with respect to argon. Both time constants and temperatures presented in these Figures are Mirels⁴ corrected.

The results from these experiments (Series I to V) indicate an average order of 0.8 for H_2 and 1.1 for Ar. Considering the uncertainty in acquiring the experimental data, an order of 1.0 may be assigned for both H_2 and Ar. Relative rate constants, k_d , may then be calculated directly from Equation (2).

$$k_{d_{\text{Rel}}} = \frac{\frac{d[H]}{dT}}{2[H_2]^{1.0} [M]^{1.0}} \quad (7)$$

An Arrhenius plot of these relative rate constants for experiments, Series I to V, is presented in Figure III. An activation energy of 85 kcal is defined by this representation. However, this value will increase when absolute rate constants are determined. This effect is explained by the fact that the absorption coefficient of H atoms is inversely proportional to both the relative rate constant and the temperature. Therefore, when absolute rate constants are calculated, the slope of the Arrhenius plot, Figure III will increase and thus define an activation energy greater than 85 kcal.

The preliminary results of these experiments may be compared with the recent results of Myerson and Watt¹ and Breshears and Bird.² As of this time the only comparison possible is through apparent activation energies. The value of 85 kcal obtained in this experiment agrees quite well with Myerson and Watt's¹ value of 93 kcal and the value of 89 kcal obtained by Breshears and Bird.

References

1. A. L. Myerson and W. S. Watt, J. Chem. Phys. 49, 425 (1968).
2. W. D. Breshears and P. F. Bird, Paper presented at the Fourteenth Symposium on Combustion, University Park, Pennsylvania, August, 1972.
3. J. V. Michael, et al. 1971-72 Annual Progress Report AEC-COO-3242-4.
4. H. Mirels, Phys. Fluids 9, 1907 (1966).

Figure Captions

- Fig. I: A plot of relative $\log \left(\frac{dH}{dT} \right)$ vs. $\frac{1}{T}$ for series I (□), Series II (○), and Series III (△). The reaction order for H_2 is computed from the distance between parallel lines.
- Fig. II: A plot of relative $\log \left(\frac{dH}{dT} \right)$ vs. $\frac{1}{T}$ for Series III (△), Series IV (⊗), and Series V (⊠). The reaction order for Ar is computed from the distance between parallel lines.
- Fig. III: A plot of relative $\log k_d$ vs. $\frac{1}{T}$ for Series I - V. The activation energy is computed from the slope of the line.

Fig. 1

Fig. II

Fig. III

-51-

Table I

Series	Composition %		Initial Pressure (mm Hg)	Shock Temperature (°K)
	H ₂	Ar		
I	.063	99.937	19 ± 1	1900 - 2400
II	.146	99.854	19 ± 1	1900 - 2500
III	.500	99.500	19 ± 1	1900 - 2500
IV	.977	99.023	10 ± 1	1800 - 2400
V	.298	99.802	32 ± 1	2000 - 2300

E. Experiment E

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

Introduction

The apparatus for kinetic studies with a coupled discharge flow reactor - T.O.F. mass spectrometer has been described previously;¹⁻³ the emphasis of the kinetic experiments performed during the past year has been on the acetylene-hydrogen atom reaction system. Results of three isotopic variations of this system have been reported previously;⁴ the results of a fourth variation are reported here along with a summarization of the implications of this extensive accumulation of data on the reaction kinetics of the acetylene-hydrogen atom reaction system. An instrument modification that allowed the use of a low pressure atomic resonance lamp as the source of ionizing radiation in the T.O.F.M.S. is also described briefly.

a) H + C₂D₂

The H + C₂D₂ reaction was investigated under acetylene-rich and acetylene-lean conditions, and the reaction was found to be first-order in both [H] and [C₂D₂]. Product profiles for the reaction were obtained under the two isolation conditions; the results for the acetylene-rich reaction at 1 and 5 torr are shown in Figures 1 and 2. The major products of the reaction are C₂HD, HD, and D; small amounts of C₂H₂ and D₂ are also observed at long reaction times.

Because of the large contribution of H₂ to the m/e = 2 peak, the concentration of deuterium atoms could not usually be observed directly, but was inferred from a relation derived from mass balance considerations:

$$[D] = [C_2HD] + 2[C_2H_2] - [HD] - 2[D_2] \quad (I)$$

This expression was confirmed experimentally at 1 torr by reducing the TOFMS sensitivity for H₂ relative to the sensitivity for deuterium atoms; this adjustment

was accomplished by reducing the energy of the ionizing electrons from the normal 18.6 eV needed to insure ionization of H_2 (I.P. = 15.4 eV) to 14 eV.

At 1 torr, the initial rate of C_2HD formation is seen to be about twice the initial rates of D and HD formation. These observations are consistent with the following two reaction channels:

where both proceed at about equal rates. As the reaction proceeds, the ratio $\frac{\Delta[HD]}{\Delta[C_2HD]}$ increases, the net production of D slows down, and other products (D_2 and C_2H_2) appear. This is caused by secondary reactions of D and C_2HD .

At 5 torr, the initial rate of HD and C_2HD formation are more nearly equal and as a result, the inferred rate of production of D is correspondingly lower. These observations are consistent with the proposed reaction channels (1) and (2) if the rate of the first process is $0.6/1.4 = 0.43$ times that of the second.

These observations can be contrasted to the results⁴ of the reaction $D + C_2H_2$ where the initial overall reaction can be attributed to the single reaction channel

at both 1 and 5 torr. The different behavior of these two systems implies that the major reactions in the $D/C_2H_2/He$ system at pressures less than 7 torr involve the formation of an addition complex that undergoes rapid unimolecular decomposition with the net result of isotope exchange; whereas, the reaction scheme of the $H/C_2D_2/He$ system apparently involves two processes. The $H/C_2D_2/He$ system exhibits the characteristics of both an isotope exchange process and a process involving pressure stabilization of the initially formed radical and subsequent reaction with another H atom.

More detailed calculations are in progress in an effort to explain the observed behavior of both systems in terms of a consistent RRKM model.

The acetylene-lean reaction is characterized by isotopic exchange similar to that observed in the $D + C_2H_2$ reaction; the reaction is observed to involve consecutive first order isotopic exchange. The major reactions affecting acetylene distribution appear to be

Since depletion of $[C_2D_2]$ was observed to be first order in $[C_2D_2]$ and $[H]$ and since the only apparent channel for removal of $[C_2D_2]$ appears to involve formation of C_2HD , it is reasonable to assume that reaction (5) is first order in both $[C_2HD]$ and $[H]$. Under the further assumption that $[H]$ is constant the two reactions can be abbreviated in the form

where A, B, and C represent C_2D_2 , C_2HD , and C_2H_2 respectively, and the primed first-order rate constants are equated with the unprimed bimolecular rate constants times $[H]$.

The concentrations of A, B, and C at any time were expressed in terms of their initial concentrations and a concentration vs. time profile was calculated; the variable parameter used in the calculation of the profiles is defined as

$$n \equiv k'_B/k'_A \quad (II)$$

The other parameters were determined as follows: $[C_2HD]_0$ and $[C_2H_2]_0$ are measured values of $[C_2HD]$ and $[C_2H_2]$ at some early point in the reaction defined as time zero; k'_A is determined from the slope of a logarithmic plot of $[C_2D_2]$ vs. dwell time; and $[C_2D_2]_0$ is obtained from the intercept of this plot and the defined time zero.

The observed profiles for pressures of 1 and 5 torr are shown in Figures 3 and 4 together with profiles calculated for a value of $n = 0.52$; an average value of $n = 0.50 \pm .05$ is obtained for the pressure range of 1 to 5 torr. A similar average value of $n' = 0.53 \pm .05$ was obtained for the atom-rich reaction of D + C_2H_2 where

$$n' = k_B''/k_A''; \quad (III)$$

A' , B' , and C' represent C_2H_2 , C_2HD , and C_2D_2 respectively; and k_A'' , k_B'' are defined in a similar manner as k_A' , k_B' .

These relationships imply that the previously undertermined rate constants for the processes:

under atom-rich conditions at pressures of 1 to 5 torr are approximately one-half of the measured rate constants for the processes:

The apparent rate constants for reaction (4) under both atom-rich and atom-lean conditions are tabulated in Table 1 and are presented as a function of the total pressure in Figure 5 along with acetylene-rich results of Michael and Niki⁵ and Hoyermann, et al.⁶ The apparent rate constants for reaction (9) have previously been reported.⁴

b) TOFMS Modification

Because of the possibility that a particular radical can be produced in the presence of large amounts of reactants whose mass spectra mask that of the radical,

it is advantageous to use an ionization source in the mass spectrometer that is sufficiently energetic to ionize the radical but not energetic enough to ionize the interfering species. Low pressure atomic resonance lamps can be used as sources of mono-energetic photons; and the energy spread of this resonance radiation is very much smaller than that attainable with the ionizing electron beam in the TOFMS. Preliminary investigations³ have demonstrated the feasibility of using an argon resonance lamp as the source of ionizing radiation in the mass spectrometer.

References

1. J. V. Michael, et al. 1968-69 Annual Progress Report AEC-NYO-3794-7.
2. J. R. Barker, D. G. Keil, J. V. Michael, and D. T. Osborne, J. Chem. Phys. 52, 2079 (1970).
3. D. G. Keil, Ph.D. Thesis, Carnegie-Mellon University 1973.
4. J. V. Michael, et al. 1971-72 Annual Progress Report AEC-COO-3242-4.
5. J. V. Michael and H. Niki, J. Chem. Phys. 46, 4969 (1967).
6. K. Hoyer mann, H. Gg. Wagner, J. Wolfrum and R. Zellner, Ber. Bunsenges Phys. Chem. 75, 22 (1971).

Figure Captions

Fig. 1: Product profiles for the reaction $H + C_2D_2$ in acetylene- d_2 -rich conditions. $P_T = 0.97$ torr; $[C_2D_2]_0 = 7.5 \times 10^{14}$ molecule cm^{-3} . The size of the points indicates relative uncertainty in concentration.

○ - $[H]$; □ - $[C_2HD]$; - $[HD]$; - $[D_2]$; - $[C_2H_2]$; ▽ - inferred $[D]$ (see text).

Fig. 2: Product profiles for the reaction $H + C_2D_2$ in acetylene- d_2 -rich conditions.

$P_T = 4.93$ torr; $[C_2D_2]_0 = 4.45 \times 10^{14}$ molecule cm^{-3} . The size of the points indicates the relative uncertainty in concentration. ○ - $[H]$; □ - $[C_2HD]$; - $[D_2]$; - $[C_2H_2]$; ▽ - inferred $[D]$ (see text); - $[HD]$.

Fig. 3: Acetylene product profiles for the atom-rich $H + C_2D_2$ reaction.

$P_T = 1.01$ torr; $[H]_0 = 9.89 \times 10^{14}$ atom cm^{-3} . ○ - $[C_2D_2]$; □ - $[C_2HD]$; - $[C_2H_2]$; △ - $[C_2D_2] + [C_2HD] + [C_2H_2]$. Calculated profiles are shown for $n = 0.52$ (see text).

Fig. 4: Acetylene profiles for the atom-rich $H + C_2D_2$ reaction. $P_T = 5.02$ torr; $[H] = 8.83 \times 10^{14}$ atom cm^{-3} . ○ - $[C_2D_2]$; □ - $[C_2HD]$; - $[C_2H_2]$; △ - $[C_2D_2] + [C_2HD] + [C_2H_2]$. Calculated profiles are shown for $n=0.52$.

Fig. 5: Plot of apparent bimolecular rate constants for the $H + C_2D_2$ reaction as a function of total pressure. Error bars indicate 10% uncertainty.

- k_{app}^H (atom-lean reaction); ○ - $k_{app}^{C_2D_2}$ (atom-rich reaction); △ - results of Michael and Niki⁵ for k_{app}^H ; - results of Wagner and coworkers for k_{app}^H extracted from a graph in reference 6.

Fig. 5

Table 1

Apparent Rate Constants for $\text{H} + \text{C}_2\text{D}_2$ at Different PressuresA. Excess $[\text{C}_2\text{D}_2]$

$P_T(\text{torr})$	$[\text{H}]_0 \text{ atoms/cm}^3$	$k_{\text{app}}^{\text{H}} \times 10^{+14} (\text{cm}^3/\text{molecule sec})$
1.21	6×10^{13}	6.6
2.11	4×10^{13}	7.9
3.20	5×10^{13}	8.5
3.91	6×10^{13}	9.0
5.62	1×10^{14}	9.7

B. Excess $[\text{H}]$

$P_T(\text{torr})$	$[\text{C}_2\text{D}_2]_0 (\text{molecules/cm}^3)$	$k_{\text{app}}^{\text{C}_2\text{D}_2} \times 10^{+14} (\text{cm}^3/\text{molecule sec})$
1.01	7×10^{12}	3.5
1.01	3×10^{13}	4.1
1.04	2×10^{13}	3.8
2.01	1×10^{13}	4.8
2.03	3×10^{13}	4.7
2.94	2×10^{13}	5.2
4.04	1×10^{13}	4.7
4.11	1×10^{13}	5.9
4.90	6×10^{13}	5.1
5.02	2×10^{13}	5.8

F. Experiment F

Absolute Quenching Cross Sections of $\text{Hg}(^3\text{P}_1)$ with Various Molecules

The development of a steady state photolytic experiment for the determination of quenching cross sections of $\text{Hg}(^3\text{P}_1)$ with various molecules was described in the 1971-72 Annual Progress Report.¹ Preliminary results for quenching by molecular hydrogen were also presented. During the past year the apparatus was modified and kinetic parameters were obtained for a wide variety of quenching species. These include H_2 , O_2 , CO , NO , N_2O , HD , D_2 , C_2H_2 , C_2H_4 , C_3H_6 , cis- $2\text{-C}_4\text{H}_8$ and n- C_4H_{10} . A brief discussion of this work is presented here.

Experimental

A description of the original configuration of the apparatus may be found in the 1971-72 Annual Progress Report.¹ Detection of 2537 Å mercury resonance emission was accomplished indirectly by the observation of the red scintillation from a #2030 Corning glass filter with a HTV-R136 photomultiplier tube. In an attempt to increase the sensitivity of the measurement by direct observation of the 2537 Å emission, this tube was replaced with an R.C.A. 1P28 photomultiplier tube. The red filter was removed and a broadband UV filter was placed between the cell and the photomultiplier housing. This filter exhibited a peak transmittance of 83% at 3300 Å and approximately 30% transmittance at 2537 Å. A schematic diagram of the apparatus is presented in Figure 1.

The mercury atom concentration in the cell was regulated by the temperature of an adjacent trap which contained a drop of mercury. Calibration of the transmittance (I/I_0) to the mercury concentration was accomplished by the use of slush baths at different temperatures. The atom concentration was calculated from the vapor pressure of Hg at these various temperatures. I_0 was measured with a liquid nitrogen bath on the trap.

The ability to maintain low mercury concentrations is of primary importance in this work. The effect of desorption of mercury from the walls of the initially well-cleaned photolysis cell was examined by closing off the cell after evacuation of mercury with liquid nitrogen on the trap. After 15 minutes, no appreciable change in either the transmitted intensity or emission intensity occurred. As a result, the effect of desorption from the walls on the regulation of the atom concentration was considered to be negligible.

For a typical quenching experiment, mercury is initially removed from the cell by cooling the adjacent trap with liquid nitrogen. The liquid nitrogen bath is replaced by a dry ice-acetone slush bath in order to avoid condensation of the quenching gas and still maintain a low mercury concentration. The quenching gas is admitted to the cell and the pressure is measured to within 10μ with a calibrated tilting McCleod gauge. Initial output from the photodetection devices is measured and the bath is removed. As the trap warms, mercury diffuses into the cell and the photocurrents are recorded with continuous variation in the mercury concentration. The duration of a typical run is only several minutes and thus facilitates repetition for improved statistics.

Results

The results of a typical experiment in the absence of added gas are presented in Figure 2. As mercury diffuses into the cell the intensity of the transmittance light decreases and the emission intensity increases. The plot is linear at high transmittance and becomes curved with decreasing transmittance. The curvature is considered to occur due to radiation imprisonment and also an end-on phenomena in which the incident light is absorbed in a region closer to the front window of the cell as the mercury concentration increases. As this becomes more pronounced, less of the emitted light is received by the photomultiplier. The effect of quenching is also illustrated in Figure 2. Competitive collisional quenching of

the excited atoms results in a decreased emission intensity for a given absorbed intensity, hence a more negative slope.

The experimental data has been integrated in terms of a modified Stern-Volmer equation. This is derived from rate equations for species in the reaction mechanism:

where the last reaction represents all possible quenching processes. The details of this derivation have been presented previously.¹ The modified Stern-Volmer equation is of the form:

$$i_a/i_f = C(1 + k_q/k_f [Q]). \quad (\text{I})$$

i_a and i_f are the measured photocurrents which correspond to the absorbed and emitted intensities respectively. C is a proportionality constant.

Error in this experiment would result from radiation imprisonment inhomogeneity in the distribution of mercury in the cell and excessive accumulation of product during a run. These problems have been considered elsewhere.² It has been determined that at the conditions of these experiments the phenomena occur to a negligible extent. Also band emission from mercury-quencher excimers would perturb the measurement of the emission intensity. Of the molecules examined in this study, only CO and $n\text{-C}_4\text{H}_{10}$ have exhibited this emission. The reported intensity and frequency distribution^{3,4} in these cases led us to assume negligible contribution to the emission intensity.

Sample results from the quenching experiment of H_2 with direct observation of the emission intensity are presented in Table I. The i_a/i_f value for a single

run has been obtained from plots such as Figure 2 as the negative of the least squares slope in the linear region, i.e., $I/I_0 > 85\%$. All i_a/i_f values for experiments at a particular pressure of quencher have been averaged over three to four runs. The uncertainty represents the standard deviation obtained from the residuals from the mean.

The photocurrent ratios (i_a/i_f) are then least squares fit to a straight line as a function of $[Q]$ with each point weighted by the inverse of the variance. The Stern-Volmer plots for H_2 , O_2 and CO are presented as examples in Figure 3. The ratio of the slope to intercept from these fits yields the ratio, k_q/k_f according to Equation (I). Since radiation imprisonment is negligible, k_f is the inverse of the natural lifetime of $Hg(^3P_1)$. The most recent determinations have produced an average value of 1.14×10^{-7} sec for this lifetime. The quenching cross section, σ_q^2 , is calculated from k_q with the simple collision theory expression

$$\sigma_q^2 = k_q \left[\frac{8\pi kT}{\mu} \right]^{-\frac{1}{2}} \quad (II)$$

μ is the reduced mass for the mercury-quencher collision. The experimental quenching rate constants and cross sections are tabulated in Table II. The uncertainty in k_q represents the standard deviation calculated from the estimated standard deviations in the slope and intercept from the least squares fit.

Discussion

The quenching parameters of Table II include several values for the quenching of mercury by H_2 . Value I of $11.3 \pm 0.4 \text{ \AA}^2$ was determined with detection of the emission intensity by the red scintillation technique. With direct observation of the 2537 $\text{\AA}$ emission, a value (II) of $11.1 \pm 0.4 \text{ \AA}^2$ was obtained. A subsequent determination (III) of $9.8 \pm 0.4 \text{ \AA}^2$ provides an indication of the precision with which quenching cross sections can be determined here. All values compare favorably with the cross section of $10.8 \pm 0.4 \text{ \AA}^2$ from this laboratory as determined

in the steady state photolytic experiment with Lyman- α photometric detection of H atom concentrations.⁶

Determination of quenching cross sections by measurement of the attenuation of emission intensity with increased pressure of added gas is defined as a "physical" method. In this work, the concentrations of mercury are sufficiently low that radiation imprisonment is negligible. The high Hg concentrations of the early physical measurements in an experiment originally described by Zemansky⁷ necessitated theoretical interpretation of the effect of imprisonment. Hence, ambiguities in the imprisonment theory were introduced into the cross section determination. Since the difference in cross sections from a Zemansky type experiment and those from this study can be attributed only to imprisonment (which is constant for both experiments), comparison on a relative basis should show agreement. In Table III, the cross sections are presented relative to that for CO. Excellent agreement between the values for H_2 , O_2 , $n-C_4H_{10}$, C_4H_8 and C_2H_2 is obtained. Also the relative values for C_2H_4 and C_3H_6 may be considered to agree within the limits of experimental uncertainty. NO and D_2 provide the only inconsistencies although the recent study of Hong and Mains⁸ indicates the original Zemansky type cross section⁹ to be in error.

The absolute cross sections for H_2 , O_2 , N_2O , C_2H_4 and $n-C_4H_{10}$ compare favorably with those reported by Yarwood, Strausz and Gunning¹⁰ from a Zemansky type experiment. Holstein theory was used to correct this data for imprisonment. It has been indicated previously^{6,10} that at the conditions of a typical Zemansky experiment, Holstein theory adequately accounts for imprisonment. This is supported by the results of the present study. Good agreement has also been obtained in comparisons with other studies at low imprisonment conditions.²

The chemical method of Cvetanovic produces quenching cross sections relative to that for N_2O . Previously a value of 12.6 Å^2 for the cross section of N_2O has

been used to calculate absolute cross sections from these ratios. However, a cross section of $21.2 \text{ \AA}^2$ has been observed in this study. The absolute cross sections for H_2 , C_2H_4 , C_3H_6 and C_4H_{10} which are derived from the relative ratios of the chemical method are presented in Table IV. The results obtained with the present value of $\sigma_{\text{N}_2\text{O}}^2 = 21.2 \text{ \AA}^2$ agree quite well with the experimental cross sections for C_2H_4 , C_3H_6 and $n\text{-C}_4\text{H}_{10}$. However, the cross section for H_2 from chemical data is slightly lower than the $10.7 \text{ \AA}^2$ value of this study. Also presented is a comparison with the cross section for NO obtained from the chemical method of Cundall and Palmer¹² based on the cis-trans isomerization of cis 2- C_4H_8 . A value of $39 \text{ \AA}^2$ had been used previously for the cross section of cis 2- C_4H_8 . If the $69.7 \text{ \AA}^2$ value from this study is used for cis 2- C_4H_8 , an absolute cross section of $41.1 \text{ \AA}^2$ results from Cundall and Palmer's ratio. This does not agree with the $28.3 \text{ \AA}^2$ cross section from the present experiment.

In summary, the quenching of $\text{Hg}(^3\text{P}_1)$ by various molecules has been examined. The very low Hg concentrations in these experiments has obviated adjustment for imprisonment and consequently has afforded a more accurate determination of total absolute cross sections for a wide variety of quenching species. Furthermore since a large number of chemical cross sections relative to that of N_2O have been measured, the value of $21.2 \text{ \AA}^2$ obtained in this work will allow accurate specification of many more cross sections than have been measured here. The availability of accurate kinetic parameters for the quenching reactions of $\text{Hg}(^3\text{P}_1)$ is of importance in studies of other transient species in mercury photosensitization as well as for comparison purposes in theoretical and mechanistic interpretation of this energy transfer progress. It is our hope that these results will contribute to further elucidation of these interactions.

References

1. J. V. Michael, et al. 1971-72 Annual Progress Report, AEC-COO-3242-4.
2. G. N. Suess, Ph.D. Thesis, Carnegie-Mellon University, 1973.
3. S. Penzes, O. P. Strausz and H. E. Gunning, J. Chem. Phys. 45, 2322 (1966).
4. O. P. Strausz, J. M. Campbell, S. De Paoli, H. S. Sandhu and H. E. Gunning, J. Am. Chem. Soc. 95, 732 (1973).
5. A. Lurio, Phys. Rev. 140, A1505 (1965).
6. J. V. Michael and C. Yeh, J. Chem. Phys. 53, 59 (1970).
7. M. W. Zemansky, Phys. Rev. 36, 919 (1930).
8. J. Hong and G. J. Mains, private communication.
9. M. G. Evans, J. Chem. Phys. 2, 445 (1934).
10. A. J. Yarwood, O. P. Strausz and H. E. Gunning, J. Chem. Phys. 41, 1705 (1964).
11. R. J. Cvetanovic, J. Chem. Phys. 23, 1203; 1208 (1955).
12. R. B. Cundall and T. F. Palmer, Trans. Faraday Soc. 56, 1211 (1960).
13. K. Yang, J. Am. Chem. Soc. 87, 5294 (1965).
14. Y. Rousseau and H. E. Gunning, Can. J. Chem. 41, 465 (1963).

Figure Captions

Fig. I: Schematic Diagram of the Apparatus. M, low pressure mercury lamp; C, reaction cell; P_1 and P_2 , phototubes; E_1 and E_2 , electrometers; R_1 and R_2 , potentiometric recorders; F, filters; L, quartz lenses.

Fig. II: Plot of Transmitted Intensity Against the Emission Intensity.
The right hand ordinate gives the equivalent $[\text{Hg}] \times l$ ($l = 3 \text{ cm}$) which corresponds to the percent transmittance on the left hand ordinate.

Fig. III: Stern-Volmer Plots for H_2 , O_2 and CO.

 

[illegible]

 

Fig. 1

Fig. 2

Fig. 3

Table I: Photocurrent Ratio (i_a/i_f) as a Function of Hydrogen Gas

P_{H_2} (torr)	$i_a/i_f \times 10^4$
0.	$4.23 \pm .48$
0.	$4.20 \pm .29$
.16	$5.47 \pm .35$
.20	$6.06 \pm .24$
.27	$6.37 \pm .30$
.33	$7.33 \pm .52$
.48	$8.72 \pm .39$
.54	$9.19 \pm .80$
.66	10.7 ± 0.8
.90	12.8 ± 1.6
1.02	13.7 ± 0.9

Table II: Quenching Rate Constants and Cross Sections

Q		$k_q \times 10^{10}$ (cc molecule ⁻¹ sec ⁻¹)	$\sigma_q^2 (\text{\AA}^2)$
H_2	I	$6.27 \pm .24$	11.3 ± 0.4
	II	$6.15 \pm .20$	11.1 ± 0.4
	III	$5.48 \pm .22$	9.8 ± 0.4
HD		$4.59 \pm .51$	10.0 ± 1.1
D_2		$3.42 \pm .20$	8.6 ± 0.5
O_2		$3.57 \pm .22$	23.9 ± 1.5
CO		$1.17 \pm .15$	7.4 ± 1.0
NO		$4.36 \pm .12$	28.3 ± 0.8
N_2O		$2.77 \pm .15$	21.2 ± 1.1
C_2H_2		$6.45 \pm .56$	39.4 ± 3.4
C_2H_4		$6.27 \pm .33$	39.6 ± 2.1
C_3H_6		$6.49 \pm .59$	48.5 ± 4.4
cis-2- C_4H_8		$8.28 \pm .24$	69.7 ± 2.0
n- C_4H_{10}		$0.80 \pm .24$	6.9 ± 2.0

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Table III: Comparison of Quenching Cross Section Relative to σ_{CO}^2 .

<u>Q</u>	<u>This Work</u>	<u>Zemansky Type Experiment</u>
H ₂	1.5	1.5
D ₂	1.2	2.1
O ₂	3.2	3.4
NO	3.8	6.0
C ₂ H ₂	5.3	5.6
C ₂ H ₄	5.4	6.4
C ₃ H ₆	6.6	7.4
2-C ₄ H ₈	9.5	9.5
n-C ₄ H ₁₀	.97	.93

Table IV: Comparison with Cross Sections from Chemical Methods^a.

	<u>H₂</u>	<u>C₂H₄</u>	<u>C₃H₆</u>	<u>n-C₄H₁₀</u>
This Work	10.7 ± 0.5 ^b	39.6 ± 2.1	48.5 ± 4.4	6.9 ± 2.0
Relative to N ₂ O	(Ref. 13)	(Ref. 11)	(Ref. 14)	(Ref. 11)
$\sigma_{\text{N}_2\text{O}}^2 = 12.6 \text{ \AA}^2$	5.3	22	29.8	3.6
$\sigma_{\text{N}_2\text{O}}^2 = 21.2 \text{ \AA}^2$	8.9	37	50.1	6.1

NO

This Work	28.3 ± 0.8
Relative to 2-C ₄ H ₈	(Ref. 12)

$\sigma_{\text{C}_4\text{H}_8}^2 = 39 \text{ \AA}^2$	23
$\sigma_{\text{C}_4\text{H}_8}^2 = 69.7 \text{ \AA}^2$	41.1

^aAll numbers in units of $\text{\AA}^2$ ^bThis is the average of the three values for H₂ in Table II.

G. Experiment G.

Theoretical Calculations

Application of the RRKM Theory of Unimolecular Reactions to the $\text{H} + \text{C}_2\text{H}_4/\text{He}$, $\text{D} + \text{C}_2\text{D}_4/\text{He}$, and $\text{D} + \text{C}_2\text{H}_4/\text{He}$ Chemical Activation Systems.

Introduction

The quantum statistical RRKM theory of unimolecular reactions has been applied to the decomposition of vibrationally excited ethyl radicals. Specifically, this theory has been used to examine the pressure dependence of the apparent bimolecular rate constant for the $\text{H} + \text{C}_2\text{H}_4$ chemical activation system with SF_6 as the collisional deactivating third body species. The experimental pressure fall-off behavior of the rate constant for this reaction system was used to assist in the final assignment of the activated complex parameters. These parameters were systematically varied until good agreement was obtained between the calculated pressure fall-off behavior and data from this laboratory for the $\text{H} + \text{C}_2\text{H}_4/\text{SF}_6$ reaction. The final parametric assignments were then used in theoretical calculations of the absolute unimolecular rate constants for decomposition at higher temperatures for comparison with thermal decomposition data for ethyl radicals from other laboratories^{1,2}. The agreement with the experimental data was quite good; the model parameters and the results of these calculations have been reported both in a previous Annual Progress Report³ and in the literature⁴. Thus the correlation of experimental data for both chemical activation and thermal activation of ethyl radicals has been successfully demonstrated with application of the same specified model in RRKM theoretical calculations.

In view of the resulting success of the theoretical predictions of experimental data, it was decided to further test the predictive ability of the specified models with unimolecular theory and attempt to gain a greater understanding of isotope effects in chemical activation systems. For this purpose

the RRKM theory has also been applied to several isotopic variations of vibrationally excited ethyl radicals. Specifically, the $\text{H} + \text{C}_2\text{H}_4$, $\text{D} + \text{C}_2\text{D}_4$, and $\text{D} + \text{C}_2\text{H}_4$ chemical activation systems with He as the collisional deactivating species have been examined and compared with experimental data from this laboratory. The models for the ethyl radicals and activated complexes of the deuterated variations have been designed to be totally consistent with those used previously for the completely protonated case. The results of these calculations will be discussed below.

Results and Discussion

1. $\text{H} + \text{C}_2\text{H}_4/\text{He}$

The proposed chemical activation mechanism for the $\text{H} + \text{C}_2\text{H}_4$ reaction, application of the RRKM theory to this system, and the relation between the apparent bimolecular rate constant (k_{bi}) and the unimolecular rate constant (k_{uni}) have been discussed in previous Annual Progress Reports^{3,5}. The resulting conclusion was the fact that the bimolecular and unimolecular rate constants are equivalent when reduced by their respective high pressure limits, thus

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

Therefore experimental data from the chemical activation system (k_{bi}) may be interpreted by unimolecular theory, provided that the high pressure limit of the apparent bimolecular rate constant ($= k_1$) is known. Fortunately, this data has been determined and reported in the literature^{3,4,6,7} and an average value, extracted from these three independent determinations, of 12.9×10^{-13} cc molecule⁻¹ sec⁻¹ is taken to be representative of the value for k_1 in this study.

Application of the RRKM theory to the $\text{H} + \text{C}_2\text{H}_4$ system requires specification of models for the ethyl radical and the activated complex; that is, geometric

configurations and normal mode vibrational frequencies must be assigned. The methods used to specify the models in this study are exactly analogous to those reported in the 1971-72 Annual Progress Report³ and therefore will not be discussed here. The models used in this study differ only slightly from the models proposed previously³. Moreover, the calculated fall-off behavior for the $\text{H} + \text{C}_2\text{H}_4/\text{SF}_6$ system³, and the calculated absolute unimolecular fall-off behavior at higher temperatures³ have been reproduced with the models of the present study. The grouped vibrational frequencies and calculated moments of inertia which have been used in these calculations are summarized in Table I.

Based upon these model parameters and the accepted value for k_1 , the calculated absolute fall-off behavior of the apparent bimolecular rate constant for the $\text{H} + \text{C}_2\text{H}_4$ system is shown in Figure 1. This is a plot of k_{bi} versus $\log_{10}(\beta\omega)$, where β represents the Lennard-Jones corrected collision efficiency of the deactivating third body species ($\beta = 1.00$ for all calculated fall-off curves).

In order to compare the calculated fall-off behavior with that of the experimental rate constants, the experimental pressures of the collisional deactivating third body species were converted, as before³, to the appropriate collision frequencies with the kinetic theory of gases. The pressure dependence of the apparent bimolecular rate constant for the $\text{H} + \text{C}_2\text{H}_4$ reaction has been measured in this laboratory in the presence of various third body deactivating species (H_2 , He, N_2 , Ne, Ar, Kr, and SF_6). Correction of these data for stoichiometry effects has been described and reported in the 1969-70 Annual Progress Report⁸ and also in the literature⁹. The stoichiometry corrected rate constants are identical to the apparent bimolecular rate constants (k_{bi}) of interest here for the $\text{H} + \text{C}_2\text{H}_4$ chemical activation system.

Relative collisional deactivation efficiencies (β_M) for the various third body molecules have been derived from data obtained in this laboratory⁹. The Lennard-Jones corrected collision efficiency for SF_6 is taken to be unity; that is, $\beta_{\text{SF}_6} = 1.00$. The multiplicative factors, β_M , that bring the data for the other third body species into coincidence with the SF_6 data on a collisional basis then represent the Lennard-Jones corrected efficiency factors for the strong collisional case. The relative collisional efficiency for He as the third body was reported to be $0.28 \pm .03$.⁹ Thus for the present study a collision efficiency for He as the third body deactivating species was chosen as 0.25, relative to that for SF_6 .

The stoichiometry corrected experimental bimolecular rate constants from this laboratory are shown in Figure IIA, along with the stoichiometry-free data of Kurylo, Peterson, and Braun⁶. The data compare favorably with the theoretically predicted fall-off curve (solid line).

2. $\text{D} + \text{C}_2\text{D}_4/\text{He}$

The proposed mechanism for the $\text{D} + \text{C}_2\text{D}_4$ chemical activation system is completely analogous to that for the protonated case. The $\text{D} + \text{C}_2\text{D}_4$ system differs from the completely protonated case in masses of the reacting species, moments of inertia, zero-point vibrational energies of the various species, fundamental vibrational frequency assignments, and critical energy for unimolecular decomposition of the excited ethyl radical. The differences, however, are purely mass effects, 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 of the molecule. Therefore models of the radical and complex, zero-point energy differences, and critical energy differences may be obtained for the $\text{D} + \text{C}_2\text{D}_4$ system which are totally

consistent with all of the final parametric assignments of the successful models which have been used in the completely protonated case. Consistency between models may be insured with the Teller-Redlich product rule¹⁰.

Teller and Redlich showed that for two isotopic molecules the product of the ω_i'/ω_i values for all vibrations of a given symmetry type is independent of the potential constants and depends only on the masses of the atoms and the geometrical structure of the molecule. Here, ω_i represents the (zero-order) frequency of the i th genuine vibration. For a non-linear polyatomic molecule, the product rule is given by

$$\prod_{i=1}^{3N-6} \frac{\nu_i}{\nu_i'} = \left(\frac{I_A I_B I_C}{I_A' I_B' I_C'} \right)^{1/2} \left(\frac{M}{M'} \right)^{3/2} \prod_{i=1}^N \left(\frac{m_i'}{m_i} \right)^{3/2} \quad (2)$$

where ν_i represents the experimentally observed fundamental frequency of the i th genuine vibration, I is the moment of inertia, M is the molecular weight, m_i are the masses of the N atoms in the molecule, and the primed quantities refer to the isotopically substituted molecule. On the basis of identical force fields for the isotopic molecules, the product rule should hold rigorously for the zero-order frequencies ω_i , and at least to a good approximation for the observed fundamentals ν_i for any mass difference¹⁰. Thus the product rule is a useful relationship for the determination of consistent models of a molecule and its isotopically substituted form, particularly in the case of activated complexes where experimental measurement is not possible.

The methods employed to specify the models of the active ethyl radical and the activated complex for the deuterated version are analogous to those used for the protonated case. The geometrical structures of the radical and complex are exactly the same as those assigned to the completely protonated models³. The

majority of the frequency assignments for the ethyl radical were obtained by application of the group frequency method of Pitzer¹¹ to the observed fundamentals for C_2D_4 reported by Crawford, Lancaster and Inskeep¹², and to the fundamentals for C_2D_6 reported by Herzberg¹⁰. All frequency assignments for C_2D_5 were obtained in the same way as those for C_2H_5 , with the exception of three degrees of freedom: the D_2C-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 atom. The stretching frequency was determined by treating the radical as a pseudo-diatomic molecule with the force constant reported by Purnell and Quinn¹³ in their study of the entropies of alkyl radicals. As suggested by Wilson, Decius, and Cross¹⁴, the approximate ratio for rotational frequencies may be obtained as

$$\frac{\nu_R}{\nu_R'} \approx \left(\frac{I'}{I} \right)^{1/2} \quad (3)$$

where I represents, in this case, the reduced moment of inertia for the free internal rotation. The out-of-plane bending frequency for C_2H_5 reported by Purnell and Quinn¹³ was used and the corresponding frequency for C_2D_5 was left as the unknown to be determined by application of the product rule.

For the activated complex, vibration frequencies were assigned to the normal modes of the planar ethylene fragment which are essentially the observed fundamentals of the completely deuterated ethylene molecule¹². This left three degrees of freedom yet to be determined: the frequencies of the two bending modes of the C-D reaction coordinate, which are assumed to be degenerate, and the frequency of the decomposition mode, or reaction coordinate. The reaction coordinate, written as $\nu_L^\ddagger$, is a non-genuine vibration in that it is a vibrational stretch which becomes a relative translational motion upon decomposition of the activated complex. Although there is no way to determine the absolute value of this "frequency", the

ratio of "frequencies" of the reaction coordinates for isotopically substituted species may be approximated by¹⁵

$$\frac{\nu_L^\ddagger}{\nu_L^{\ddagger'}} \approx \left[\left(\frac{1}{M_\alpha} + \frac{1}{M_\beta} \right) \left(\frac{1}{M_\alpha'} + \frac{1}{M_\beta'} \right) \right]^{1/2} \quad (4)$$

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 C-D reaction coordinate was then determined, relative to that for the protonated case, by application of the Teller-Redlich product rule.

The resulting models for the C_2D_5 radical and $C_2D_5^\ddagger$ activated complex were thus designed to be consistent with the successful models of the light ethyl radical and complex. All grouped vibrational frequency assignments and calculated moments of inertia are summarized in Table I.

Only one parameter remains to be determined for application of the RRKM theory to this system, and that is the critical energy for decomposition, E_O' . This parameter may be determined by the consideration of a slice through the potential energy surface describing this system; this slice must also contain the reaction coordinate. 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

$$V = E_O - E_Z^\ddagger + E_Z \quad (5A)$$

$$V' = E_O' - E_Z^{\ddagger'} + E_Z' \quad (5B)$$

where E_O is the critical energy for decomposition, E_Z and $E_Z^\ddagger$ are the zero-point vibrational energies of the radical and complex, respectively, and the primed

quantities refer to the isotopically substituted system. Since the potential energy surfaces for the protonated and deuterated cases are identical, or nearly so, (5A) may be equated with (5B) with the result

$$E'_0 = E_0 + \Delta E_z - \Delta E_z^\ddagger \quad (6)$$

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 models with the result that E'_0 is equal to 41.59 kcal mole⁻¹, based on the value of 40.0 kcal mole⁻¹ for the completely protonated case.

According to Equation (1), the apparent bimolecular rate constant for the $D + C_2D_4$ system (k'_{bi}) may now be predicted theoretically provided that its high pressure limit ($=k'_1$) is known. The value for k'_1 has not been determined experimentally in this laboratory and is not available in the literature. Therefore the Transition State Theory¹⁵ of reaction rates was applied in a calculation of the isotope effect for k'_1/k_1 . Transition State Theory reduces the calculation of ratios of rate constants to a calculation of ratios of isotopic partition functions. Here again, this calculation is simplified by the fact that the potential energy surfaces for isotopic molecules are the same to a very high degree of approximation. In addition to the specified parameters discussed above for C_2H_5 , $C_2H_5^\ddagger$, C_2D_5 , and $C_2D_5^\ddagger$, this calculation requires the vibration frequencies and moments of inertia for C_2H_4 and C_2D_4 . The frequencies used are the experimental values reported by Crawford *et al.*¹² and the moments of inertia were calculated on the basis of the geometrical structure for ethylene given by Herzberg¹⁰. All parameters for this calculation are summarized in Table I. The resulting ratio of rate constants, assuming equal transmission coefficients, is 0.583. Therefore, based upon the accepted value for k_1 , k'_1 is equal to 7.52×10^{-13} cc molecule⁻¹ sec⁻¹. With this

value for k_1' and the model parameters discussed above, the theoretically predicted absolute fall-off behavior of the apparent bimolecular rate constant (k_{bi}') for the $D + C_2D_4$ system is shown in Figure 1.

The pressure dependence of the apparent rate constant for the $D + C_2D_4$ reaction has been measured in this laboratory in the presence of He as the third body deactivating species; this data has been reported.¹⁶ This data has also been corrected for stoichiometry effects by the same methods which were used for the $H + C_2H_4/He$ system. The resulting stoichiometry corrected rate constants ($=k_{bi}'$) are shown in Figure IIb along with the theoretically predicted fall-off curve (dashed line). The agreement between theory and experiment is seen to be quite good.

3. $D + C_2H_4/He$

The proposed mechanism for the $D + C_2H_4/He$ chemical activation system was reported in the 1969-70 progress report,⁸ along with experimental data obtained with the TOFMS Flow System. Because of two different channels for decomposition of the excited ethyl radical and subsequent isotopic mixing, the reaction scheme for this system is much more complicated than that for the completely protonated or completely deuterated cases. The experimental results for the determination of the apparent bimolecular rate constant (k_{bi}'') as a function of pressure for the D-atom excess experiments (pseudo first order conditions) are of interest in this study. Under atom excess conditions, apparent rate constants based on C_2H_4 depletion were obtained and are shown in Figure VI of the 1969-70 progress report.⁸ Under these conditions, the following reactions are important.

With the steady state approximation for $C_2H_4D^*$ and C_2H_4D , the rate of depletion of C_2H_4 may be calculated and the apparent bimolecular rate constant is found to be

$$k_{bi}'' = k_1'' \int_{\epsilon_{ol}}^{\infty} \frac{(k_{\epsilon 2} + \omega)f(\epsilon)}{(k_{\epsilon 1} + k_{\epsilon 2} + \omega)} d\epsilon \quad (7)$$

where $k_{\epsilon 1}$ and $k_{\epsilon 2}$ are the specific rate constants for dissociation of radicals, with active internal energy ϵ , by D-atom and H-atom fragmentation, respectively; ϵ_{ol}'' is the critical energy for dissociation of radicals by Reaction II, ω is the collision frequency of the excited radicals with the third body species, and $f(\epsilon)$ represents the normalized distribution function for the formation of excited ethyl radicals by Reaction I. In the low pressure limit ($\omega \rightarrow 0$), equation (7) reduces to

$$k_{bi}'' = k_1'' \langle k_{\epsilon 2} / (k_{\epsilon 1} + k_{\epsilon 2}) \rangle \quad (8)$$

and in the high pressure limit ($\omega \rightarrow \infty$), equation (7) reduces to

$$k_{bi}'' = k_1'' \quad (9)$$

Application of unimolecular theory to the $D + C_2H_4$ system involves the evaluation of the integral in equation (7). Here again, models must be specified for the radical and complexes. For this case, however, in addition to the model for the active ethyl radical, $C_2H_4D^*$, 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 for the complex which describes the decomposition of $C_2H_4D^*$ by H-atom dissociation, $C_2H_3D \cdots H^\ddagger$, must also be specified. The methods employed to specify these models are exactly analogous to those used for the completely protonated and completely deuterated cases, and therefore will not be discussed here. As was done with the $D + C_2D_4$ case, consistency between models for the mixed isotope version, $D + C_2H_4$, and the $H + C_2H_4$ case was insured with the Teller-Redlich product rule.¹⁰

The resulting models for C_2H_4D , $C_2H_4 \cdots D^\ddagger$, and $C_2H_3D \cdots H^\ddagger$ were therefore also designed to be consistent with the successful models of the light ethyl radical and complex. All grouped vibrational frequency assignments and calculated moments of inertia are summarized in Table I.

The RRKM theory was then applied, as before, to evaluate the energy dependent terms (k_{e1} , k_{e2} , and $f(\epsilon)$) of the integral in equation (7); the integral was then evaluated graphically. The resulting values of k_{e1} and k_{e2} , the specific rate constants for dissociation of ethyl- d_1 radicals by D-atom and H-atom rupture, respectively; and $f(\epsilon)$, the distribution function of excited ethyl radicals, are plotted as a function of the active energy (ϵ) of the $C_2H_4D^*$ radicals in Figure III. For any particular energy of interest ϵ , the absolute values of the decomposition rate constants (k_{ei}) are shown on the left ordinate and the corresponding value of the distribution function is shown on the right ordinate in Figure III. The critical energies for decomposition by D-atom rupture, ϵ_{o1}'' , and for decomposition by H-atom rupture, ϵ_{o2}'' , are shown on the abscissa in Figure III. As was done for the $D + C_2D_4$ system, critical energies for the decomposition modes of the $D + C_2H_4$ system were calculated with equation (6); the zero-point energies were obtained from the specified models in Table I with the result that $\epsilon_{o1}'' = 41.76$ kcal mole $^{-1}$ and $\epsilon_{o2}'' = 39.98$ kcal mole $^{-1}$. Again, these values are based on the value of 40.0 kcal mole $^{-1}$ for the completely protonated case.

According to equations (7) and (9), the apparent bimolecular rate constant for the $D + C_2H_4$ system (k_{bi}'') may now be predicted theoretically, provided that its high pressure limit ($=k_1''$) is known. Since the value for k_1'' is not available, the Transition State Theory¹⁵ was applied in a calculation of the isotope effect for k_1''/k_1 ; this calculation is analogous to that described for k_1'/k_1 , where k_1' is the high pressure limit for the completely deuterated case. All parameters required for this calculation are summarized in Table I. The resulting ratio

of rate constants, assuming equal transmission coefficients, is 0.503. Therefore, based upon the accepted value of k_1 for the completely protonated case, k_1'' for $D + C_2H_4$ is equal to 6.49×10^{-13} cc molecule $^{-1}$ sec $^{-1}$. With this value for k_1'' in equation (7) and the model parameters listed in Table I, the theoretically predicted absolute fall-off behavior of the apparent bimolecular rate constant (k_{bi}'') for the $D + C_2H_4$ system has been calculated and is shown in Figure I. The theoretically predicted fall-off curve (dotted line) is also shown in Figure IIC, along with the low pressure (1-4 torr in He) stoichiometry-free bimolecular rate constants ($=k_{bi}''$) obtained in this laboratory.⁸ Although there is considerable scatter in the experimental data, the agreement between theory and experiment is, once again, satisfactory.

The fall-off behavior for the $D + C_2H_4$ chemical activation system, however, is strikingly dissimilar to the fall-off behaviors for the $H + C_2H_4$ and $D + C_2D_4$ systems in that it is relatively insensitive to pressure (or collision frequency). As shown in Figures I and II, the completely protonated and completely deuterated versions show a marked pressure fall-off behavior whereas the predicted bimolecular rate constant for the mixed isotope case is nearly independent of pressure. This striking difference seems at first sight, puzzling; however, the insensitivity of k_{bi}'' to changes in pressure (ω) may be completely understood by examination of equations (7) through (9) and Figure III. From equation (7) it may be seen that if $k_{e2} \gg k_{e1}$, such that $(k_{e1} + k_{e2} + \omega)$ could be replaced by $(k_{e2} + \omega)$, then equation (7) would reduce to equation (9) for any value of ω ; thus k_{bi}'' would be equal to k_1'' for any value of ω and the pressure fall-off curve would be strictly flat and constant. This is nearly the case and the reasons for it are as follows. For any given energy ($\geq \epsilon_{o1}''$) of the $C_2H_4D^*$ radical the specific rate of decomposition by H-rupture (with rate constant k_{e2}) is favored both statistically and energetically over that for decomposition by D-rupture (with rate constant k_{e1}).

On a purely statistical basis, consideration of the excited ethyl radical, $\text{CH}_2\text{-CH}_2\text{D}^*$, leads to the conclusion that k_{e2} is greater than k_{e1} by a factor of 2 since there are two rupturable H-atoms and only one rupturable D-atom. Thus $k_{e2}/k_{e1} = 2$ on statistical considerations alone; this ratio of two is always present at any energy and is hence independent of temperature and pressure.

In addition, H-atom rupture from the hot $\text{C}_2\text{H}_4\text{D}^*$ radical is energetically favored over D-atom rupture. The chemically activated radicals, $\text{C}_2\text{H}_4\text{D}^*$, are energized by at least an amount equal to ϵ_{o1}'' ; if the reactants, $\text{D} + \text{C}_2\text{H}_4$, possess the average thermal energy $\langle \epsilon_{th} \rangle$ at the reaction temperature of interest, then the average total energy possessed by the active radical is

$$\langle \epsilon \rangle = \epsilon_{o1}'' + \langle \epsilon_{th} \rangle \quad (10)$$

According to RRKM theory, k_{ei} is proportional to the fraction of the number of states of the excited species ($\text{C}_2\text{H}_4\text{D}^*$) at energy ϵ that occur as an activated complex at energy $\epsilon_i^\ddagger$, subject to the energy equivalence relation

$$\epsilon = \epsilon_{o1}'' + \epsilon_i^\ddagger \quad (11A)$$

Thus for the H-atom decomposition channel,

$$\epsilon = \epsilon_{o1}'' + \epsilon_1^\ddagger \quad (11B)$$

and for the D-atom decomposition channel,

$$\epsilon = \epsilon_{o2}'' + \epsilon_2^\ddagger \quad (11C)$$

Upon equating equations (11B) and (11C), one finds that

$$\epsilon_{o1}'' - \epsilon_{o2}'' = \epsilon_2^\ddagger - \epsilon_1^\ddagger \quad (12)$$

The difference in critical energies has already been determined as 1.78 kcal mole⁻¹, hence

$$\epsilon_2^\ddagger = \epsilon_1^\ddagger + 1.78 \text{ kcal mole}^{-1} \quad (13)$$

Therefore, for any given energy $\epsilon (= \epsilon_{01}'' + \chi)$ k_{e1} is evaluated at $\epsilon_1^\ddagger = \chi$ and k_{e2} is evaluated at $\epsilon_2^\ddagger = \chi + 1.78 \text{ kcal mole}^{-1}$. Hence for any particular energy of the hot ethyl radical, there is more energy available for decomposition by C-H bond fission and k_{e2}/k_{e1} is again a number greater than one.

For example, examination of Figure III shows that $f(\epsilon)$ is at its maximum value ($= 0.40$) for an energy $\epsilon = 43 \text{ kcal mole}^{-1}$, and the ratio of k_{e2}/k_{e1} at this energy is equal to 12.8. At $53 \text{ kcal mole}^{-1}$ the ratio k_{e2}/k_{e1} is equal to 3.7; however, the value of the distribution function at this energy has dropped to 3×10^{-5} . If the contribution of the statistical factor is taken out of these ratios, then $k_{e2}/k_{e1} = 6.4$ and 1.85 at energies corresponding to 43 and $53 \text{ kcal mole}^{-1}$, respectively. These ratios are now on a purely energetic basis. The origin of this energetic effect lies in the difference in the vibrational frequencies and zero-point energies of the two activated complexes.

Evaluation of equation (8) and comparison with equation (9) has shown that, even in the low pressure limit, the bimolecular rate constant k_{bi}'' is 90% of the way to its high pressure limit k_1'' . Thus the average value of the ratio k_{e2}/k_{e1} is found to be 9.0 for the reaction temperature of interest, 298°K , in this study. Since k_{e2} is greater than k_{e1} by a factor of 9 on the average, the initial hypothesis that $k_{e2} \gg k_{e1}$ is nearly met and as a result the pressure fall-off curve for the $\text{D} + \text{C}_2\text{H}_4$ system is nearly flat. As seen in Figure I there is a slight pressure fall-off in the region corresponding to a collision frequency of 10^8 to 10^9 sec^{-1} . From Figure III, it may be seen that $f(\epsilon)$ is at its highest values for values of k_{e2} between 10^8 and 10^9 sec^{-1} . This is why the slight pressure fall-off occurs in this region.

It is also of interest to note that $f(\epsilon)$ is a strong function of temperature and that the distribution function broadens with increasing temperature. Hence for higher temperatures, according to equations (10) and (11), k_{e2} and k_{e1} would

be evaluated at greater energies than those considered in this study. It is evident from Figure III that the ratio k_{e2}/k_{e1} decreases with increasing energy of the hot radical. Thus at very high temperatures, the relative energetic differences between the two decomposition modes would become insignificant and k_{e2}/k_{e1} would approach the limiting statistical factor of 2. Evaluation of equation (8) for this limiting value of the ratio would then show that k_{b1}'' would be 66.7% of the way to its high pressure limit k_1'' .

References

1. M. C. Lin and M. H. Back, Can. J. Chem. 44, 505 (1966).
2. L. F. Loucks and K. L. Laidler, Can. J. Chem. 45, 2795 (1967).
3. J. V. Michael, et al. 1971-72 Annual Progress Report AEC-COO-3242-4.
4. J. V. Michael and G. N. Suess, J. Chem. Phys. 58, 2807 (1973).
5. J. V. Michael, et al. 1970-71 Annual Progress Report AEC-NYO-3794-13.
6. M. J. Kurylo, N. C. Peterson, and W. Braun, J. Chem. Phys. 53, 2776 (1970).
7. J. A. Eyre, T. Hikida, and L. M. Dorfman, J. Chem. Phys. 53, 1281 (1970).
8. J. V. Michael, et al. 1969-70 Annual Progress Report AEC-NYO-3794-11.
9. J. V. Michael, D. T. Osborne, and G. N. Suess, J. Chem. Phys. 58, 2800 (1973).
10. Infrared and Raman Spectra, G. Herzberg (D. Van Nostrand Co., Inc., 1947), pp. 232, 344, 439.
11. K. S. Pitzer, Chem. Rev. 27, 39 (1940).
12. B. L. Crawford, Jr., J. E. Lancaster, and R. G. Inskeep, J. Chem. Phys. 21, 678 (1953).
13. J. H. Purnell and C. P. Quinn, J. Chem. Soc. (Lond.), 4049 (1964).
14. Molecular Vibrations, E. B. Wilson, Jr., J. C. Decius, and C. P. Cross (McGraw-Hill Book Co., New York, 1955), p. 184.
15. J. Bigeleisen and M. Wolfsberg, Adv. Chem. Phys. 1, pp. 17-30 (1958).
16. J. V. Michael, et al. 1968-69 Annual Progress Report AEC-NYO-3794-7.

Figure Captions

Fig. I: Theoretically predicted fall-off behavior of the apparent bimolecular rate constants for:

- (1) $\text{H} + \text{C}_2\text{H}_4$ (solid line)
- (2) $\text{D} + \text{C}_2\text{D}_4$ (dashed line)
- (3) $\text{D} + \text{C}_2\text{H}_4$ (dotted line)

Fig. II: Comparison between theory and experiment of the fall-off behavior of the apparent bimolecular rate constants for:

A. $\text{H} + \text{C}_2\text{H}_4$ (solid line is theoretically predicted)

- experimental data of Braun⁶ and co-workers for $\text{H} + \text{C}_2\text{H}_4$ in He.

- data^{5,9} from this laboratory for $\text{H} + \text{C}_2\text{H}_4$ in He, from the Real Time Lyman- α experiments.

- data^{5,9} for $\text{H} + \text{C}_2\text{H}_4$ in He, from the Lyman- α Flow System.

- data^{5,9} for $\text{H} + \text{C}_2\text{H}_4$ in He, from the TOFMS Flow System.

- data^{5,9} for $\text{H} + \text{C}_2\text{H}_4$ in SF_6 , from the Real Time Lyman- α experiment.

B. $\text{D} + \text{C}_2\text{D}_4$ (dashed line is theoretically predicted)

- data¹⁶ for $\text{D} + \text{C}_2\text{D}_4$ in He, from the Real Time Lyman- α experiment.

C. $\text{D} + \text{C}_2\text{H}_4$ (dotted line is theoretically predicted)

- data⁸ for $\text{D} + \text{C}_2\text{H}_4$ in He (in D atom excess experiments), from the TOFMS Flow System.

Note: All experimental points in Fig. II are either stoichiometry-free or stoichiometry-corrected.

Fig. III: Plots of k_{e1} , k_{e2} , and $f(e)$ versus e , the energy of the active ethyl radical $\text{C}_2\text{H}_4\text{D}^*$.

Fig. II

14

12

10

8

6

4

2

0

$R_{1/2} (\times 10^3) = \text{cc molec. sec.}^{-1}$

$\log_{10} (P/P_0)$

$H + C_2H_4$

$D + C_2D_4$

$D + C_2H_4$

Fig. II Plots of $k_b (\times 10^{13}) \text{ cc molecule}^{-1} \text{ sec}^{-1}$ vs. $\log_{10} (P_w)$

Fig. III

Table I. Parameter Assignments

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		
	1429 (4)						
	1037 (2)						
	988 (2)						
	485 (1)						
C ₂ H ₅ [‡]	3047 (4)	36.21	35.11	12.81	--	40.00	6
	1467 (3)						
	1023 (2)						
	973 (3)						
	100 (2)						
C ₂ D ₅	2222 (5)	57.68	51.83	16.78	3.81		
	1075 (4)						
	823 (2)						
	785 (2)						
	350 (1)						
C ₂ D ₅ [‡]	2275 (4)	53.60	52.19	24.84	--	41.59	6
	1188 (3)						
	795 (2)						
	742 (3)						
	69 (2)						
C ₂ H ₄ D	2841 (5)	42.94	40.30	10.04	2.08		
	1341 (4)						
	1029 (2)						
	954 (2)						
	432 (1)						

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 ₄D [‡]	3047 (4)	43.54	36.79	18.46	--	41.76	2
	1467 (3)						
	1023 (2)						
	973 (3)						
	85 (2)						
C ₂ H ₃ D....H [‡]	2854 (4)	39.04	38.47	14.08	--	39.98	4
	1398 (3)						
	966 (2)						
	915 (3)						
	96 (2)						
C ₂ H ₄	3047 (4)	33.85	28.09	5.76	--		
	1470 (3)						
	1023 (2)						
	973 (3)						
C ₂ D ₄	2275 (4)	49.41	37.90	11.51	--		
	1191 (3)						
	795 (2)						
	742 (3)						