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SHOCK-TUBE STUDY OF THE REACTION $H + O_2 + Ar \rightarrow HO_2 + Ar$

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SUMMARY

Rate coefficient data for the recombination reaction $H + O_2 + Ar \longrightarrow HO_2 + Ar$ have been determined from studies of lean hydrogen-oxygen mixtures behind incident shock waves over the temperature range of 948 to 1125 K. Hydroxyl radical concentration profiles were measured by ultraviolet absorption spectroscopy, and rate data were obtained through analysis of induction time and exponential growth parameter data. Analysis of the data yielded the rate coefficient 2.3×10^{15} cm^6/mole^2-sec which is generally lower than most of the more recent values obtained from shock-tube studies. The effect of boundary-layer formation on the conditions behind the shock was also examined and found to be negligible.

INTRODUCTION

When hydrogen and air are suddenly heated as in a supersonic combustor, ignition is preceded by a relatively short period, commonly called the induction period, during which there is a rapid buildup of free radical concentration with very little heat release. Studies (refs. 1 to 4) of the hydrogen-oxygen reaction have established that the induction period consists of a short initiation period during which small concentrations of free radicals are produced, followed by the bulk of the period during which the concentration of the free radicals increases exponentially at essentially constant temperature and pressure. The dominant reactions during the induction period are

$$H_2 + O_2 \xrightarrow{k_1} OH + OH \qquad \text{I}$$

$$OH + H_2 \xrightarrow{k_2} H_2O + H \qquad \text{II}$$

$$H + O_2 \xrightarrow{k_3} OH + O \qquad \text{III}$$

$$O + H_2 \xrightarrow{k_4} OH + H \qquad \text{IV}$$

where k_i are the corresponding rate coefficients. At low temperatures and high pressures ($T \leqq 1200$ K and $P \geqq 1$ atmosphere), the radical recombination reaction

$$H + O_2 + M \xrightarrow{k_5} HO_2 + M \qquad \text{V}$$

where M is any third body, becomes important and is primarily responsible for long induction times (ref. 5).

One parameter which must be taken into consideration in the design of a supersonic combustor, especially for operation at low temperatures and high pressures, is the induction time, that is, the time between sudden heating of the hydrogen-air mixture and the onset of ignition. The induction time can be calculated (ref. 5) provided a set of elementary reactions and the corresponding rate coefficients accurately representing the detailed chemical processes are known. The hydrogen-oxygen mechanism is well known, and the rate coefficients for reactions I to IV are known reasonably well (refs. 6 to 9). At present the rate coefficient for reaction V is known only to within a factor of 2 (ref. 7). Since this reaction is important at low temperatures and high pressures, accurate rate coefficient data are required to calculate reasonably accurate induction times.

The purpose of this study was to obtain an accurate rate coefficient for reaction V at temperatures below 1200 K and pressures of 1 atmosphere and greater. Rate information on reaction V was obtained from measurements of induction times and the rate of exponential growth of the hydroxyl radical concentration behind shock waves. The induction time and the exponential growth are related to the rates of the reactions occurring during the induction period and have been used to determine rate coefficients (refs. 8 and 9). The experiments were carried out with hydrogen-oxygen mixtures diluted with argon at reaction pressures from 1.00 to 1.27 atmospheres. The concentration of OH was measured by ultraviolet absorption spectroscopy.

SYMBOLS

k_1, k_2, k_3, k_4, k_5	rate coefficients, centimeters^3/mole-second for bimolecular reactions and centimeters^6/mole^2-second for termolecular reactions
P	pressure, atmospheres
P_1, Q_1	spectroscopic notation for OH molecular band system
R	universal gas constant
T	absolute temperature, K

λ	exponential growth parameter, second^{-1}
τ	induction time, microseconds

EXPERIMENTAL APPARATUS AND PROCEDURE

All data were obtained behind incident shock waves in an 8.9-cm internal-diameter stainless steel shock tube. The tube has a 214-cm-long driver section and a 580-cm-long driven section. Mylar diaphragms clamped between the driver and driven sections were ruptured by increasing the pressure in the driver section beyond their yield strength. Helium-nitrogen gas mixtures served as the driver gas. The speed of the shock wave was measured with a raster system (ref. 10) upon which timing marks were superimposed at 10-μsec intervals. Test gas mixtures were prepared by the method of partial pressures from commercial hydrogen (99.9 percent), dry oxygen (99.6 percent), and argon (99.995 percent) without further purification.

For the measurement of OH concentration profiles a lamp containing a trace amount of water vapor in an argon carrier gas powered by a 100-watt 28-MHz radio-frequency oscillator was used as a source of characteristic OH radiation. Radiation from the lamp was made parallel before entering the shock tube, and the emerging light was focused onto the entrance slit of a 1/2-meter Czerny-Turner type of monochromator with a 1200-lines/mm grating blazed at 3000 Å. The monochromator was set to pass a region containing the $Q_1(1)$ to $Q_1(6)$ lines and the $P_1(1)$ and $P_1(2)$ lines (see ref. 11). Although other lines are also present in this region, the ones mentioned contribute more than 99 percent of the recorded light. The light from the exit slit of the monochromator was detected by a 9558 Q photomultiplier, and the resulting signal was fed to an oscilloscope. Additional details on the absorption technique for measuring OH concentrations are given in reference 11.

Experiments were carried out by using lean H_2-O_2-Ar gas mixtures the compositions of which are given in table I. The initial test gas pressure for all the runs was 80 mm Hg. Data on the absorption by OH as a function of time were read from oscillograms, such as figure 1, with an optical comparator. The signal-to-noise ratio of this absorption trace is characteristic of that obtained for all runs. Absorption data were reduced to a concentration of OH by using the calibration curves described in reference 11. From each run the following parameters were determined: (1) An induction time τ, defined as the time interval between shock heating and the attainment of an OH concentration of 1×10^{-10} mole/cm^3; and (2) the exponential growth parameter λ, which is a measure of the rate of exponential growth of the free radical concentration. The exponential growth parameter was defined as $\lambda \equiv \frac{d \log_e [OH]}{dt}$ and was obtained from semilog plots of OH concentration against the particle time t. A typical OH concentration profile and the measured parameters τ and λ are shown in figure 2.

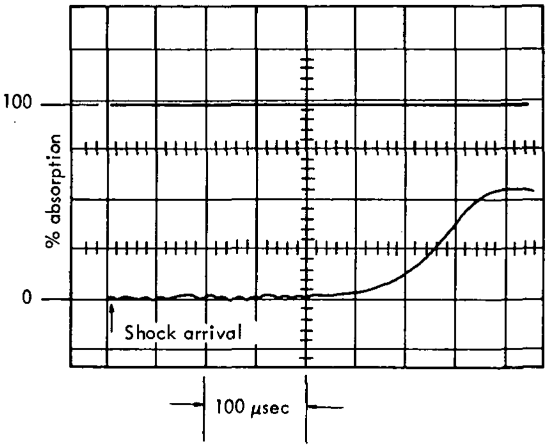

Figure 1.- Oscillogram tracing of an OH absorption profile for a 1% H_2-4% O_2-95% Ar gas mixture. T = 975 K.

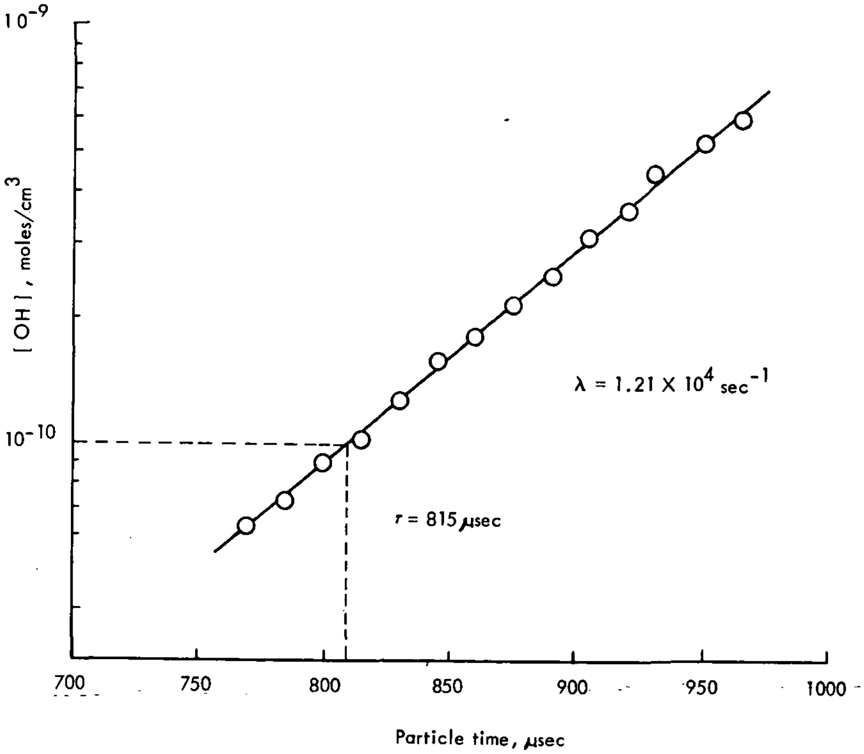

Figure 2.- OH concentration profile for a 1% H_2-4% O_2-95% Ar gas mixture. T = 975 K.

CONSIDERATION OF BOUNDARY-LAYER EFFECTS

Prior to the analysis of the data, consideration was given to the possibility that boundary-layer growth might make the ideal shock-wave assumptions invalid at long observation times. Such boundary-layer effects would tend to increase the temperature and density of the gas as well as make the ideal relation between particle time and laboratory time invalid (refs. 12 and 13).

A series of runs were made by using a 7-percent N_2O—93-percent Ar gas mixture in which the concentration of the N_2O was monitored by absorption spectroscopy. The gas N_2O was used because it does not dissociate to any significant extent below 1200 K, and in addition it provided a continuum absorption spectrum with a suitable absorption coefficient for the pressure conditions of these experiments. The test gas pressure in these runs was 80 mm Hg, and the temperature immediately behind the shock front ranged from 810 to 1100 K. The background light source was a water-cooled lamp containing a trace amount of CO in an argon carrier gas. The lamp was powered by a radio-frequency oscillator and produced an intense CO band in the region of the N_2O absorption continuum (1800 Å). The lamp was calibrated by using the known temperature and N_2O concentration immediately behind the shock front. Beer's law (ref. 14) was used to relate the absorbance to the N_2O concentration and to determine the absorption coefficient.

The N_2O absorption profile obtained in each run displayed the same qualitative features. The absorption by N_2O after passage of the shock wave remained constant for times much longer than the observation periods in the H_2-O_2-Ar experiments. Near the contact surface the absorption began to increase. At the contact surface the measured absorption was about 2 percent larger than the amount of absorption at the shock front. For the temperatures and densities given in reference 13, the absorption by N_2O at the contact surface should have been about 14 percent larger than at the shock front if boundary-layer effects were significant. On the basis of these results ideal shock-wave conditions were assumed to be maintained at least over the periods where the OH measurements were made. Accordingly, the analysis of the data was carried out by using the ideal shock relations.

DATA ANALYSIS

The induction time and the exponential growth parameter data obtained from the H_2-O_2-Ar experiments are listed in table I and plotted (open circles) in figures 3 and 4 as a function of the reaction temperature. The experimental error in τ and λ is estimated to be ±15 percent. In order to obtain rate coefficient data on the reaction $H + O_2 + Ar \longrightarrow HO_2 + Ar$, the data in table I were compared with calculated induction times and exponential growth parameters. The calculated values were obtained from

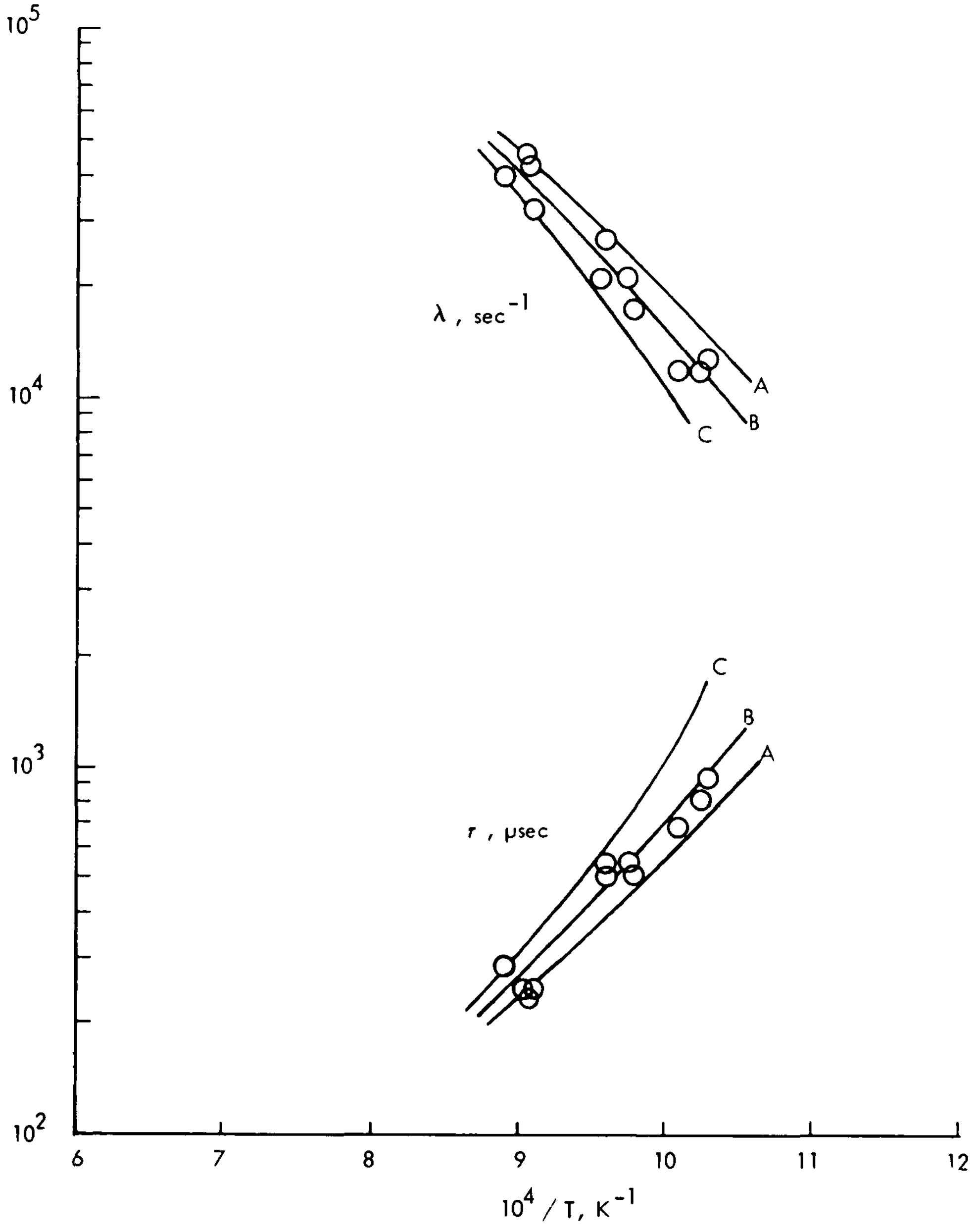

Figure 3.- Comparison of experimental data with computed curves based on various rate coefficients for reaction V for 1% H_2-4% O_2-95% Ar mixture. A, k_5 (M = Ar) = 1.3×10^{15}; B, k_5 (M = Ar) = 2.3×10^{15}; C, k_5 (M = Ar) = 3.5×10^{15} in units of $cm^6/mole^2$-sec.

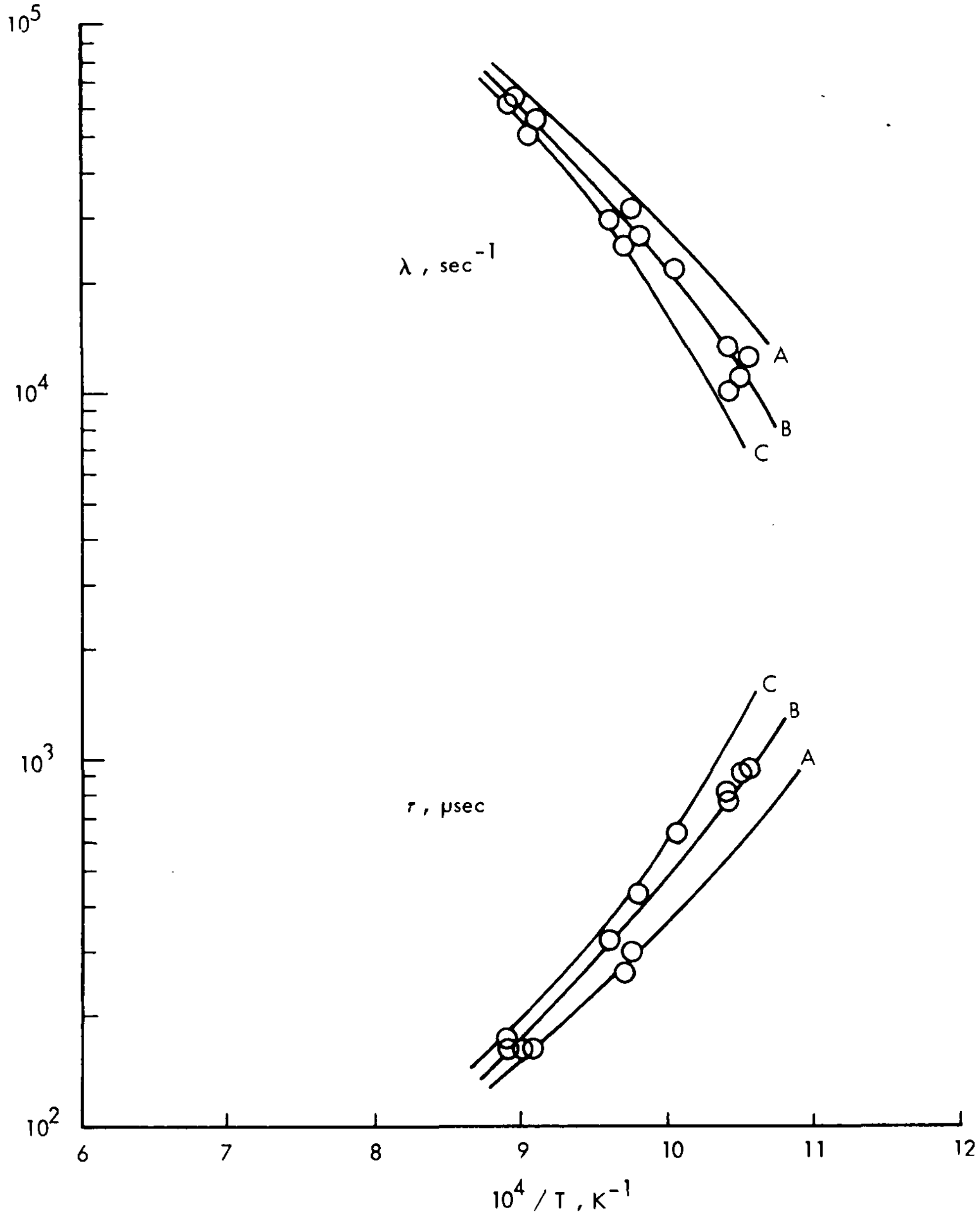

Figure 4.- Comparison of experimental data with computed curves based on various rate coefficients for reaction V for 1% H_2-8% O_2-91% Ar mixture. A, k_5 (M = Ar) = 1.3×10^{15}; B, k_5 (M = Ar) = 2.3×10^{15}; C, k_5 (M = Ar) = 3.5×10^{15} in units of cm^6/mole^2-sec.

OH concentration profiles which were determined by integrating a set of rate equations which describe the rate of growth of free radicals during the initial stages of the H_2-O_2 reaction. The set of rate equations was integrated on a computer by using a modified Runge-Kutta scheme with a variable step size. The reaction scheme used in the analysis included reactions I to V. In this method of analysis rate coefficients must be assumed for reactions I to IV. The rate coefficients used in the analysis were taken from references 8, 9, and 15 and are

$$k_1 = 1.79 \times 10^{13}\exp\left(-\frac{48\ 200}{RT}\right) \tag{1}$$

$$k_2 = 2.3 \times 10^{13}\exp\left(-\frac{5200}{RT}\right) \tag{2}$$

$$k_3 = 9.9 \times 10^{13}\exp\left(-\frac{14\ 700}{RT}\right) \tag{3}$$

$$k_4 = 7.5 \times 10^{13}\exp\left(-\frac{11\ 100}{RT}\right) \tag{4}$$

in units of cm^3/mole-sec.

Induction time and exponential growth parameter curves were calculated for a variety of assumed values for k_5. In these calculations the relative third-body efficiencies for H_2, O_2, and Ar were taken from reference 7. The results of several of these calculations are shown in figures 3 and 4 (solid-line curves). The best fit to the data was given by

$$k_5\ (M = Ar) = 2.3 \times 10^{15} \tag{5}$$

in units of $cm^6/mole^2$-sec for the temperature range of 948 to 1125 K. With an experimental error of ±15 percent for τ and λ, the error in k_5 was estimated to be ±20 percent.

The value of k_5 obtained by the preceding method is also highly dependent on the value of the rate coefficient chosen for reaction III and to a lesser extent on the rate coefficient chosen for reaction IV. Consequently, consideration must be given to the reliability of the values for k_3 and k_4 in the temperature range of the present study. In comparison with recent studies (refs. 16 to 19) and the values compiled by the Leeds group (refs. 6 and 7), the uncertainty for k_3 and k_4 is estimated to be about ±15 percent and

±30 percent, respectively. With these uncertainties for k_3 and k_4 and the ±15-percent error in τ and λ, the uncertainty in k_5 (M = Ar) is about ±40 percent.

COMPARISONS WITH OTHER SHOCK-TUBE STUDIES

The other shock-tube studies of reaction V were carried out at temperatures higher than that of the present study; therefore, comparisons can only be made with extrapolated values.

Gutman and others (ref. 18) obtained data on reaction V in the temperature range of 1018 to 1285 K by monitoring behind a reflected shock the oxygen atom increase during the induction period of the H_2-O_2 reaction. They reported the mean value k_5 (M = Ar) = 3.3×10^{15} $cm^6/mole^2$-sec with an experimental error of ±30 percent. Browne and others (ref. 17) obtained data on reaction V from a shock-tube study of the H_2-CO-O_2 system over the temperature range of 1400 to 3000 K. They reported the expression k_5 (M = Ar) = 3.2×10^{12} T^{-1} $cm^6/mole^2$-sec which gives values that are about 40 percent larger than equation (5) in the temperature range of the present experiments. Getzinger and Blair (ref. 20) obtained the value k_5 (M = Ar) = 2.2×10^{15} $cm^6/mole^2$-sec from a shock-tube study of the H_2-O_2 recombination zone at temperatures between 1259 and 1912 K. In a similar but more recent study over the temperature range of 1435 to 1868 K, Blair and Getzinger (ref. 21) reported the value k_5 (M = Ar) 3.0×10^{15} $cm^6/mole^2$-sec with a standard deviation of 1.3×10^{15}. The Leeds report (ref. 7) recommends the expression k_5 (M = Ar) = 1.59×10^{15} exp(1000/RT) $cm^6/mole^2$-sec for the temperature range of 300 to 2000 K. At 1000 K this expression gives a value about 10 percent larger than equation (5). As these comparisons indicate, the rate coefficient determined in this study is generally lower than the values determined from other shock-tube studies.

CONCLUDING REMARKS

The radical recombination reaction $H + O_2 + Ar \longrightarrow HO_2 + Ar$ has been studied in lean hydrogen-oxygen mixtures over the temperature range of 948 to 1125 K for reaction zone pressures of about 1 atmosphere. The experimentally determined induction times and exponential growth parameter data were satisfactorily correlated with a kinetic model by using the temperature independent rate coefficient 2.3×10^{15} $cm^6/mole^2$-sec. This value is lower than most of the values obtained from recent shock-tube studies. Because of the dependence of the method of analysis on the values selected for the reactions $H + O_2 \longrightarrow OH + O$ and $O + H_2 \longrightarrow OH + H$ this value is only considered to be accurate to within ±40 percent. For the experimental conditions of this study the effect of boundary-layer formation on the conditions behind the shock wave was found to be negligible.

Langley Research Center,
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Hampton, Va., October 6, 1972.

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TABLE I.- EXPERIMENTAL RESULTS

T, K	P, atm	τ, μsec	λ, sec^{-1}
Mixture: 1% H_2-4% O_2-95% Ar			
1120	1.23	289	4.07×10^4
1105	1.20	249	4.66
1100	1.20	243	3.26
1100	1.20	249	4.27
1045	1.12	522	2.12
1040	1.11	537	2.73
1026	1.08	545	2.15
1020	1.08	507	1.74
990	1.04	685	1.22
975	1.02	815	1.21
970	1.01	941	1.28
Mixture: 1% H_2-8% O_2-91% Ar			
1125	1.27	173	6.10×10^4
1120	1.26	161	6.12
1105	1.24	160	5.06
1100	1.23	162	5.65
1041	1.14	322	2.94
1032	1.13	262	2.52
1026	1.12	299	3.14
1020	1.11	430	2.66
995	1.07	636	2.16
962	1.02	761	1.36
962	1.02	797	.992
952	1.01	933	1.10
948	1.00	940	1.24

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