RATE COEFFICIENT FOR THE REACTION $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$:

RESULTS FROM 2000 TO 5300 K

Jan P. Hessler and Hong Du

Chemistry Division, Argonne National Laboratory

The new kinetic technique known as "tunable-laser flash-absorption" has recently provided an unprecedented extension of the temperature range over which the rate of the reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ has been measured. These new measurements resolve an 18-year-old controversy over the high-temperature behavior of the rate of the most important reaction in combustion. In studies supported by the Division of Chemical Sciences, Dr. Jan P. Hessler of Argonne National Laboratory and his postdoctoral associate, Dr. Hong Du, have shown that the rate of the above reaction follows a simple Arrhenius expression, $k(T) = 1.62 \times 10^{-10} \exp[-7474/T(K)] \text{ cm}^3 \text{ s}^{-1}$, from 960 to 5300 K. Previously, measurements by one group extended only up to 3300 K. At 2600 K, the highest temperature studied by three other groups, the measured rates differed by 220%. To obtain the new results a shock wave was used to quickly heat a sample and the rate of production of OH directly behind the shock wave was measured by tuning the wavelength of a pulsed dye laser to a region of strong absorption by the OH molecule. The strength of this absorption was measured as a function of distance behind the shock wave by directing the light from the laser beam onto a linear-array detector. This technique, developed by Dr. Hessler and his colleagues, is capable of measuring the rates of very fast reactions, and, thereby, is ideal for precise studies at very high temperatures where the rates of chemical reactions are the fastest. An article describing these results has been accepted for publication in the *Journal of Chemical Physics*.

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Rate Coefficient for the Reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$; Results from 2000 to 5300 K

Jan P. Hessler and Hong Du

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

The reaction between atomic hydrogen and molecular oxygen, $\text{H} + \text{O}_2 \rightleftharpoons \text{HO}_2^* \rightarrow \text{OH} + \text{O}$, is one of the most important reactions in gas-phase combustion. For example, it is important in the oxidation of H_2 , controls the chain branching in the oxidation mechanism for all hydrocarbon fuels, and is the beginning reaction in a hierarchical scheme for modeling combustion reactions in flowing systems. In spite of the importance of this reaction, there is a controversy over the temperature dependence of the rate coefficient at high temperatures. In 1973 Schott¹ deduced the temporal behavior of the oxygen concentration from measurements of the chemiluminescence from O-CO recombination (1250 to 2500 K) and found non-Arrhenius behavior of the form $T^{-0.907}$ and an activation energy, $E/k = 8369$ K. In 1985, Frank and Just² used atomic resonance absorption spectrophotometry to simultaneously measure atomic oxygen and hydrogen (1700 to 2500 K) and found Arrhenius behavior with an activation energy, $E/k = 8691$ K. The controversy is focused on the temperature dependence of the preexponential factor. In dynamic terms, at issue is the relative importance of statistical vs. nonstatistical recrossing of the transition state. Statistical recrossing arises from the ratio of probabilities for the dissociation of the intermediate complex, HO_2^* , into the forward and reverse channels, and is not important except at extremely high temperatures. Nonstatistical recrossing occurs when a significant fraction of the trajectories entering the strong interaction region do not yield products even at very low temperatures.

Since 1988, five groups have reported measurements of the rate

coefficient of this reaction at the high temperatures produced by shock tube techniques. Three have used the continuous-wave laser technique developed at Stanford University by Professor R. K Hanson (also supported by the Division of Chemical Sciences) to monitor the concentration of hydroxyl^{3,4,5} and the other two^{6,7} have used flash photolysis to produce hydrogen atoms, and follow their decay with atomic resonance absorption spectrophotometry. The experimental results agree below 1600 K, however, the temperature dependence of the preexponential factors ranges from $T^{-0.927}$ to $T^{2.0}$. Because of the different temperature dependent prefactors the results diverge significantly at high temperatures. For example, at 2600 K the extreme results differ by a factor of 2.2 and, when extrapolated to 5000 K they differ by a factor of 7.4. Clearly, measurements up to 5000 K will resolve this controversy, provide a reliable phenomenological rate coefficient, and significantly extend the data base for the reaction so that theoretical calculations of thermal rate coefficients may be tested against experimental results.

We have recently reported measurements from 2000 to 5300 K performed with the new tunable-laser flash-absorption technique⁸ developed in this laboratory. The kinetic behavior of the system was monitored by measuring the concentration of the hydroxyl radical immediately behind a shock front. The accompanying figure shows a schematic of the experimental setup. Briefly, light from a high-resolution, pulsed, dye-laser system is tuned to the center of a strong absorption line of the species of interest. This light beam is focused to produce a relatively long and uniform spatial distribution along the axis of the shock tube and is timed to traverse the shock tube when the shock front is located in front of a linear-array detector. This detector measures the transmitted energy as a function of distance along the axis of

the shock tube. When two independent light pulses are sampled, one with a shock front and the other without, the absorption coefficient as a function of the distance behind the shock front can be calculated. If the absorbing species is in thermodynamic equilibrium with the bath gas, this absorption coefficient is proportional to the concentration of the absorbing species. When enough is known about the parameters which describe the absorption process, the concentration can be calculated absolutely.

One advantage of the flash-absorption technique is the very high effective band width of the detection system. This band width determines the maximum rate of change of concentration that can be accurately measured. The flash-absorption technique acquires spatial information and converts it to temporal information through the velocity of the shock front. Therefore, the band width is determined by the width of an element on the array detector (25.4 μm) and the duration of the light pulse (16 ns). Our effective band width is greater than 60 MHz. For comparison, the band width for both the continuous-wave laser technique and atomic-resonance absorption spectrophotometry is determined by the RC time constant of the detection system. A typical 3-dB band width for monitoring a continuous-wave laser system is 150 kHz.⁴ The larger band width of the flash-absorption technique allows us to measure accurately very rapid changes in concentration. Therefore, we can perform measurements at very high temperatures where the rates of the reactions are very fast.

Even though the hydrogen/oxygen system is the simplest chemical system in combustion, under the conditions used for our experiments, the system is complex enough to require numerical solutions of the coupled differential equations used to describe its kinetic behavior. We have evaluated the

relative importance of the reactions which describe this chemical system and determined that at high temperature only the reactions $\text{H}_2 + \text{M} \rightarrow 2\text{H} + \text{M}$ and $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ determine the kinetic behavior of OH. Therefore, we may extract the rate coefficients for these two reactions from our measurements. To determine these rate coefficients we used a non-linear least-squares technique. This approach has the advantage that we may determine both the *best-fit* values of the rate coefficients and their *confidence limits*.

Our results for the *best-fit* values of the rate coefficient of the $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ reaction and their *confidence limits* are shown in the accompanying figure. The solid line represents the Arrhenious expression for the temperature dependent behavior of the rate coefficient,

$$k(T) = (1.62 \pm 0.12) \times 10^{-10} \exp[-(7474 \pm 122)/T(\text{K})] \text{ cm}^3\text{s}^{-1}$$

from 960 to 5300 K. The uncertainties are as the 95% confidence level. Our results agree to within experimental error with the results from Prof. Hanson's laboratory. We have also shown the average results obtained by other groups. The confidence limits of our measurements at the lower temperatures are approximately a factor of three smaller than the experiments of Yuan *et al*, Frank and Just, and Fujii *et al*. At high temperatures our data becomes significantly scattered with respect to the scatter at lower temperatures. This scatter is due to our uncertainty in the length of time required to heat the molecular hydrogen enough for it to produce hydrogen atoms. This effect has been observed in other systems and is a consequence of the fact that at high temperatures the rate of the chemical reactions approaches the rate of thermalization of the system. In spite of this scatter, we point out that the scatter in our high temperature results is comparable to the scatter in the low temperature results of most of the previous workers.

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The most important
reaction in the
Chemistry of Combustion

Tunable-laser Flash-absorption Technique

Rate Coefficient for $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$

$$k(T) = 1.62 \times 10^{-10} e^{-7474/T(\text{K})} \text{ cm}^3 \text{ s}^{-1}$$

from 960 to 5300 K

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