

Rate constant of $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$ from 1500 to 2000 K

W. T. Rawlins and W. C. Gardiner Jr.

Citation: *The Journal of Chemical Physics* **60**, 4676 (1974); doi: 10.1063/1.1680967

View online: <http://dx.doi.org/10.1063/1.1680967>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/60/12?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Quantum mechanical calculation of the rate constant for the reaction \$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}\$](#)

J. Chem. Phys. **100**, 733 (1994); 10.1063/1.466940

[Rate coefficient for the reaction \$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}\$: Results at high temperatures, 2000 to 5300 K](#)

J. Chem. Phys. **96**, 1077 (1992); 10.1063/1.462194

[Rate constants for the reactions \$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}\$ and \$\text{D} + \text{O}_2 \rightarrow \text{OD} + \text{O}\$ over the temperature range 1085–2278 K by the laser photolysis–shock tube technique](#)

J. Chem. Phys. **95**, 262 (1991); 10.1063/1.461483

[Pressure dependence of the absolute rate constant for the reaction \$\text{OH} + \text{C}_2\text{H}_2\$ from 228 to 413 K](#)

J. Chem. Phys. **73**, 6108 (1980); 10.1063/1.440147

[Rate constant of \$\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}\$ from 1350 to 1600 K](#)

J. Chem. Phys. **60**, 2290 (1974); 10.1063/1.1681361



Rate constant of $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$ from 1500 to 2000 K

W. T. Rawlins and W. C. Gardiner, Jr.

University of Texas, Austin, Texas 78712

(Received 7 December 1973)

It was shown several years ago that concentration profiles of the OH radical in the shock-initiated combustion of lean ($[\text{H}_2]/[\text{O}_2] = 0.1$) hydrogen-oxygen-argon mixtures at low pressures (≈ 30 kPa) and high temperatures (1200–2000 K) exhibit transient maxima prior to attainment of partial equilibrium. At that time, the maxima could not be accounted for quantitatively in terms of the accepted mechanism of the $\text{H}_2\text{-O}_2$ reaction. The profiles have been reanalyzed utilizing more sophisticated computational techniques and increased knowledge of the reaction mechanism. The occurrence of maxima at temperatures above 1500 K was found to depend upon the ratio of the rate constants of the elementary reactions $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ and $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$. Using the rate constant expression $1.6 \times 10^{14} \exp(-56.6 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the former reaction, the rate constant expression for the latter was found to be $5.5 \times 10^{13} \exp(-29 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This latter expression does not extrapolate linearly on an Arrhenius plot to the available room temperature data. The effect of boundary layer growth on the data analysis is discussed.

I. INTRODUCTION

Shock tube experiments on the hydrogen-oxygen reaction have provided information about the high-temperature rates of a number of elementary reactions.¹ Individual rate constants for the dominant bimolecular reactions



must be extracted somewhat indirectly from the experimental data, however, since in studies of induction zone behavior^{2–6} and complete density profiles,⁷ at least three approximately known rate constants must be adjusted to fit the data for limited portions of the reaction zone in which those rate constants are important. The relatively narrow range of inverse temperature for which the data analysis must be performed causes further ambiguity in the resulting rate constant expressions. (See, for example, Ref. 5.) The most directly interpretable studies have been those of the early exponential growth zone, which yield expressions for k_1 and the product $k_2 k_3$.¹ Studies of total reaction profiles usually led to confusion, since the results could not be reconciled with other work.^{8,9}

In 1968, we (GMRT)⁹ reported the existence of transient excursions above the “partial equilibrium”¹⁰ level of OH concentration in fuel-lean ($[\text{H}_2]/[\text{O}_2] = 0.1$) mixtures dilute in argon. At that time, these “spikes” could not be reproduced computationally by a kinetic mechanism in which k_1 , k_2 , k_3 , and k_8 were all compatible with other rate constant measurements, particularly of k_2 . In the present study, the same spike data have been refined and reanalyzed using better information about chain branching rates,⁵ more sophisticated computational procedures, and an expression for k_3 derived in a recent study of OH spikes observed in fuel-rich mixtures.¹¹

II. DATA ANALYSIS

The laboratory experimental details were described previously.⁹ The nominal composition of the experimental gas mixtures was $\text{H}_2:\text{O}_2:\text{diluent} = 1:10:89$, where the diluent was argon, $\text{He}:\text{Kr} = 17:72$, or $\text{He}:\text{Kr} = 24:65$. The experiments were done in incident shock waves with temperatures from 1200 to 2500 K and starting pressures of 1.3 kPa. The OH radical concentration was measured by monitoring the emission-corrected absorption of the Bi (306.7 nm) resonance line. Measurable spikes were observed below 2000 K.

The spikes can be parametrized by defining a spike ratio R and a duration D . R was originally defined by GMRT as $[\text{OH}]_{\text{max}}/[\text{OH}]_{\text{pe}}$, where $[\text{OH}]_{\text{pe}}$ is the partial equilibrium concentration of OH. At the time, it appeared plausible to associate the more or less level portion of the experimental record just after the spike with $[\text{OH}]_{\text{pe}}$ (cf. Ref. 9, Fig. 1.) We now find that this definition was actually not quite correct, since a true $[\text{OH}]_{\text{pe}}$ was usually not attained on the short time scale of the oscillographic records. Accordingly, R is redefined here as

$$R \equiv [\text{OH}]_{\text{max}}/[\text{OH}]_{\text{ex}},$$

where $[\text{OH}]_{\text{max}}$ is the maximum value of $[\text{OH}]$ and $[\text{OH}]_{\text{ex}}$ is determined, in computer experiments, by the extrapolation of a line through $[\text{OH}]$ at points 30 and 60 μs (laboratory time) after the peak back to the time of the peak. Laboratory experimental R values were re-determined from the original oscilloscope trace photographs, assuming Beer's law to be valid and using the formula

$$R = \frac{\log(1 - b/I_0)}{\log(1 - a/I_0)},$$

where I_0 is the transmitted intensity before shock arrival, a is the absorbed intensity determined by an extrapolation of the line through the transmitted intensities at points 30 and 60 μsec after the maximum deflec-

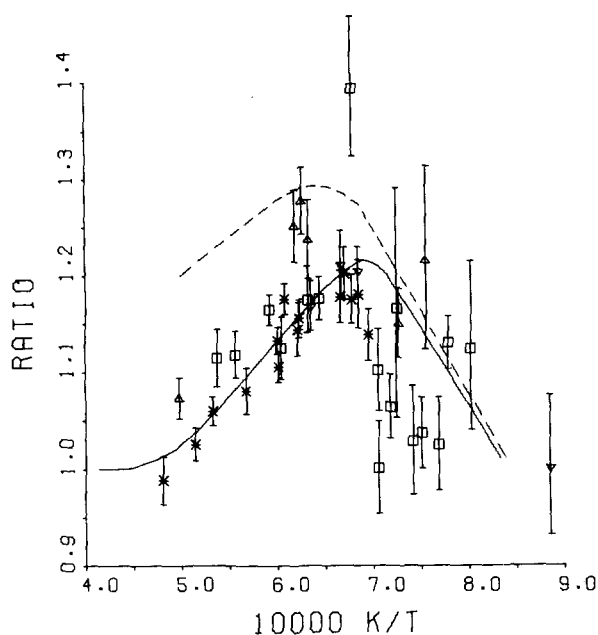


FIG. 1. Peak ratios for $\text{H}_2:\text{O}_2$:diluent=1:10:89, starting pressure 1.3 kPa. The data points correspond to mixtures as follows: \square , diluent Ar; *, diluent Ar, experimental gas admitted through a liquid nitrogen cold trap; Δ , diluent He:Kr=17:72; ∇ , diluent He:Kr=24:65. The solid curve was calculated using the rate constant set of Table I. The dashed curve was calculated using the same rate constant set except for k_8 , for which the AHW expression was used (cf. Fig. 5). The temperature used for reference is the no-reaction shock temperature.

tion back to the time of the maximum deflection, and b is the absorbed intensity at the time of the maximum spike deflection. It may be noted that the different extrapolations used in the laboratory and computer experiments are equivalent to one another only if $\epsilon I[\text{OH}]$ is small enough to permit expansion of $\exp(-\epsilon I[\text{OH}])$ to $1 - \epsilon I[\text{OH}]$ without loss of accuracy as defined by the overall accuracy of our investigation. The values of $\epsilon I[\text{OH}]$ were indeed always small enough that no systematic error was introduced through discordant extrapolations. Error bars were determined for each experimental R value on the basis of the extreme combinations of a and b that could reasonably be read from the record. The error bars are thus larger for the experiments with lower I_0 and S/N ratio. The experimental R values are plotted against inverse temperature in Fig. 1. Due to the more stringent data reduction procedures used here, there were substantially more runs that could not be analyzed, and hence fewer data points to plot, than in Ref. 9.

The spike duration D was left essentially as originally defined by GMRT, namely as the full width of the spike at half its height above the back-extrapolated level. Experimental D values are much more difficult to determine reproducibly from the experimental records than R values, and were therefore used in the present study only for a final, semiquantitative consistency check. Graphs of experimental D values are given in Ref. 9.

For comparison with the laboratory data, OH profiles and R values were generated by numerical integration

TABLE I. Mechanism and rate constant expressions.^a

Reaction	k	Reference
(01) $\text{H}_2 + \text{M} = 2\text{H} + \text{M}$	$2.23 \times 10^{12} T^{1/2} \exp(-387 \text{ kJ}/RT)$	b
(02) $\text{O}_2 + \text{M} = 2\text{O} + \text{M}$	$1.85 \times 10^{11} T^{1/2} \exp(-400 \text{ kJ}/RT)$	c
(03A) $\text{H}_2 + \text{M} = \text{H}_2^* + \text{M}$	$4.11 \times 10^{12} \exp(-208 \text{ kJ}/RT)$	d
(03B) $\text{H}_2^* + \text{O}_2 = 2\text{OH}$	$5.0 \times 10^{10} T^{1/2}$	d
(1) $\text{H} + \text{O}_2 = \text{OH} + \text{O}$	$4.0 \times 10^{13} \exp(-51.4 \text{ kJ}/RT)$	e
(2) $\text{H}_2 + \text{O} = \text{OH} + \text{H}$	$1.6 \times 10^{14} \exp(-56.4 \text{ kJ}/RT)$	see text
(3) $\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$	$5.2 \times 10^{13} \exp(-27 \text{ kJ}/RT)$	f
(4) $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	$2.0 \times 10^{15} \exp(3.6 \text{ kJ}/RT)$	g
(5) $\text{H} + \text{O}_2 + \text{H}_2\text{O} = \text{HO}_2 + \text{H}_2\text{O}$	$5.0 \times 10^{16} \exp(3.6 \text{ kJ}/RT)$	g
(6) $\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	$7.5 \times 10^{23} T^{-2.6}$	h
(7) $\text{H}_2 + \text{HO}_2 = \text{H}_2\text{O} + \text{OH}$	$2.0 \times 10^{11} \exp(-100 \text{ kJ}/RT)$	i
(8) $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$	$5.5 \times 10^{13} \exp(-29 \text{ kJ}/RT)$	see text

^aConcentration units are mol cm^{-3} .

^bA. L. Myerson and W. S. Watt, J. Chem. Phys. **49**, 425 (1968).

^cW. S. Watt and A. L. Myerson, J. Chem. Phys. **51**, 1638 (1969).

^dC. B. Wakefield, Ref. 2.

^eG. L. Schott, Ref. 5.

^fW. C. Gardiner, Jr., W. G. Mallard, and J. H. Owen, Ref. 11.

^gD. Gutman, E. A. Hardwidge, F. A. Dougherty, and R. W. Lutz, J. Chem. Phys. **47**, 4400 (1967).

^hJ. B. Homer and I. R. Hurle, Proc. R. Soc. Lond. A **314**, 585 (1970).

ⁱV. V. Voevodsky, Symp. Combust. 7th, London, Engl. 1958 (1959), p. 34.

of the coupled differential equations describing the chemical kinetics and the dynamics of shocked gas flow. The effects of boundary layer growth, found by heat transfer gauge observations to be laminar throughout the flow duration of the experiments, were taken into account by modifying the conservation equations, assuming the validity of Mirels's limiting flow equations for a laminar boundary layer.¹² The final set of elementary reactions and rate constants used to fit the experimental R data is given in Table I. The R values implied by this set are indicated by the solid curve in Fig. 1.

III. RESULTS

Preliminary calculations showed that the R values were sensitive almost exclusively to the expressions assumed for k_1 , k_2 , k_3 , and k_8 . In order to systematize the search for an optimum set of rate constant expressions, further calculations were done by using recent literature expressions as "standards" and finding the effects upon R values of varying the standard expressions. Starting expressions for k_1 , k_2 , and k_3 were taken from growth constant measurements,¹ and an expression for k_8 was derived from the work of Albers, Hoyer-mann, Wagner, and Wolfrum (AHWW)¹³ on the reverse reaction. A quantitative study of the sensitivity of calculated R values to individual rate constants was carried out by doubling and halving each rate constant expression with respect to a standard set. The results of sensitivity calculations for k_1 , k_2 , k_3 , k_8 , and recombination rates, using the final rate constant set of Table

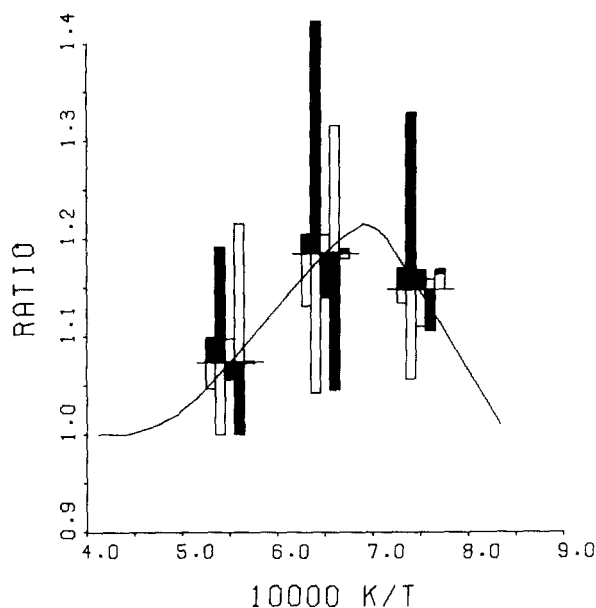


FIG. 2. Sensitivity of calculated ratios to assumed rate constant expressions. The curve was calculated using the rate constant set of Table I. The bars show the change in calculated ratios at 1820, 1540, and 1330 K when a given rate constant expression is doubled (shaded) or halved (unshaded). Starting from the left at each temperature, the bars correspond to k_1 , k_2 , k_3 , k_8 , and k (recombination reactions), respectively.

I as a standard rather than the starting set, are shown in Fig. 2. It can be seen that at temperatures above about 1500 K, the calculated spike ratios are controlled by the ratio k_2/k_8 and show a low sensitivity to k_1 and k_3 . At temperatures below 1500 K, the calculated R values are essentially sensitive to k_2 alone; comparison with Fig. 1 shows that even this sensitivity is small

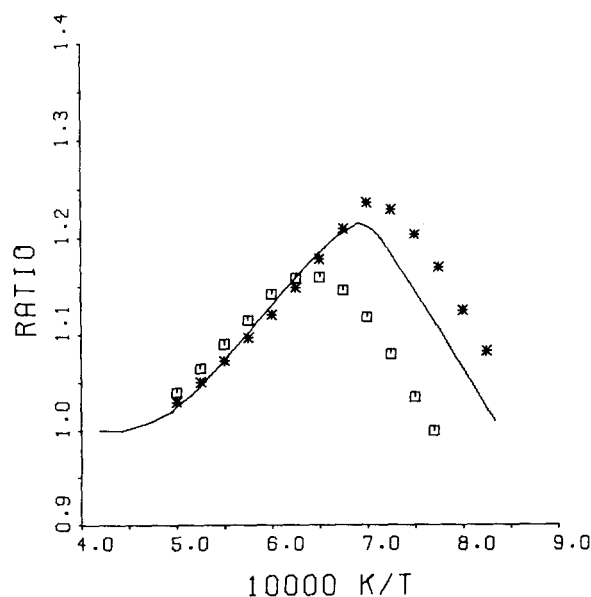


FIG. 3. Effect of assumed flow model on calculated ratios. The solid line was calculated using the assumption of limiting laminar boundary layer flow (cf. Ref. 12). The asterisks were calculated assuming turbulent boundary layer growth, and the squares were calculated assuming steady shock flow. The rate constant set of Table I was used for all calculations.

compared to the scatter of the experimental data in that temperature region. The dependence of R upon the flow model is shown in Fig. 3.

Since our previous paper,⁹ a number of shock-tube measurements of k_2 have appeared. All of them indicate that in our temperature range, k_2 is substantially larger than appeared reasonable at that time (Fig. 4). This change of consensus is what now permits a satisfactory interpretation of the lean mixture data.

The four-parameter (k_1, k_2, k_3, k_8) problem was reduced to a one-parameter one by judicious use of some previously proposed rate constant relationships. Schott's exponential growth studies give expressions for k_1 and $k_2 k_3$ directly,⁵ and recent work in this laboratory on rich mixture OH spikes yields an expression for k_1/k_3 .¹¹ The temperature ranges covered by both studies are compatible with that covered here. Combination of these experimentally determined expressions for k_1 , $k_2 k_3$, and k_1/k_3 leaves only k_8 as an unknown and insures that the rate constant set which fits lean mixture spikes will also be compatible with both rich mixture spikes¹¹ and exponential growth data.⁵ Utilizing k_1 , k_2 , and k_3 expressions determined by this procedure, the rate constant expression for Reaction (8) was adjusted until numerical integrations gave a satisfactory fit to the experimental R values above 1500 K (cf. Fig. 1). The expression thus derived is

$$k_8 = 5.5 \times 10^{13} \exp(-29 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The spike durations D computed with this set of rate constants were in satisfactory agreement with experi-

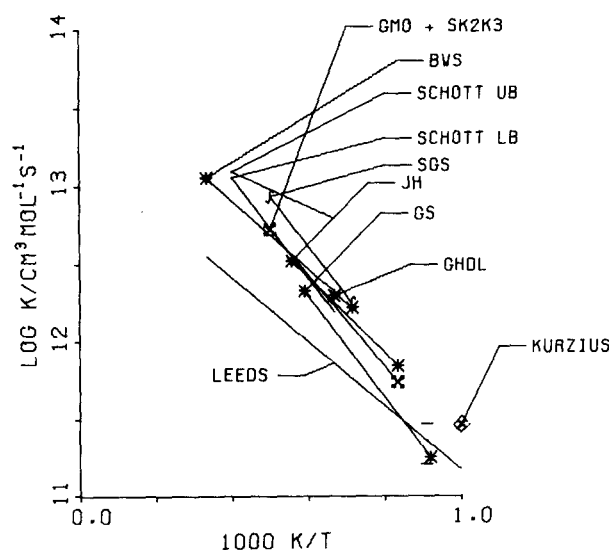


FIG. 4. Arrhenius graph for $\text{O} + \text{H}_2 = \text{OH} + \text{H}$. The symbols refer to literature data as follows: BWS, Ref. 7; GHDL, Ref. 27; GMO+SK2K3, derived by combining the results of Ref. 11 and Ref. 5, as described in the text; GS, Ref. 28; JH, Ref. 29; KURZIUS, private communication cited by D. L. Baulch *et al.*, Ref. 30; LEEDS, Ref. 30; SCHOTT LB and SCHOTT UB, lower and upper bounds given in Ref. 5; SGS, Ref. 14. The horizontal lines are error limits suggested by D. L. Baulch *et al.*, Ref. 30.

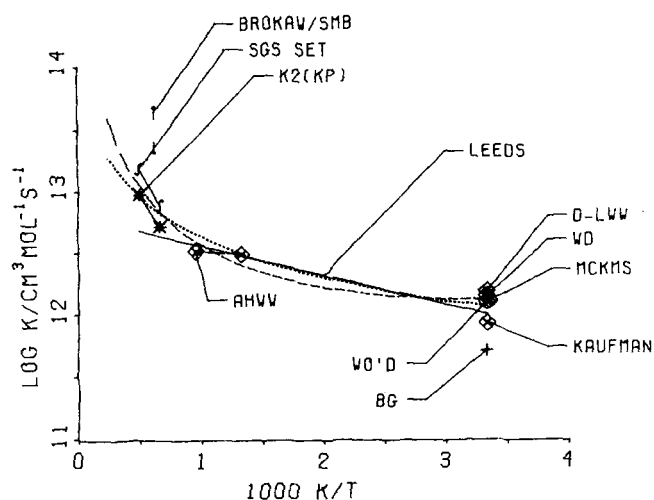


FIG. 5. Arrhenius graph for $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$. The symbols refer to literature data as follows. AHWV, Ref. 13; BG, Ref. 31; BROKAW/SMB, approximate range calculated in Ref. 21, from data in Ref. 22; D-LWW, Ref. 32; KAUFMAN, Ref. 33; K2 (KP), first evaluation of k_8 , as described in text; LEEDS, Ref. 34; MCKMS, Ref. 23; SGS SET, derived using the results in Ref. 14 for k_1/k_2 , in Ref. 11 for k_1/k_3 , and in Ref. 6 for k_1 , as described in the text; WO'D, Ref. 35; WD, Ref. 36. All of the room temperature data are derived from the decay rate of OH radicals generated by titration of H atoms with NO_2 , a system that has been subjected to serious criticism; cf. Ref. 37 and Ref. 23. The AHWV expression was derived from their results on the rate of the reverse reaction. The dashed line is a nonlinear least squares fit to the data, as described in the text, $\log k = 6.23 + 2.03 \log T + 4.99 \text{ kJ}/RT$. The dotted line is a least-squares fit to the same data with $\log k = 9.33 + 1.11 \log T$. The BG datum was revised upwards to $\log k = 11.95$, see Ref. 38.

ment. Data scatter allows a tolerance of at most $\pm 25\%$ for this determination. The corresponding expression for the ratio k_2/k_8 is $2.9 \exp(-27 \text{ kJ}/RT)$. An Arrhenius graph of k_8 is shown in Fig. 5.

These expressions are based on the expressions for k_1 and $k_2 k_3$ given by the O-atom growth constant measurements of Ref. 5. A more recent determination of these expressions was made by H_2O growth constant measurements (GBO).⁶ The selection of k_1 does not affect the determination of k_2/k_8 as long as an expression for k_3 is used such that the ratio k_1/k_3 given by Ref. 11 is preserved. This can be seen from the low, reciprocal sensitivity of calculated R values to k_1 and k_3 above 1500 K shown in Fig. 2. Therefore, adoption of k_1 (GBO) in place of k_1 (Ref. 5) does not affect the above k_2 and k_2/k_8 expressions. However, coupling the resulting k_3 to the GBO product $k_2 k_3$ gives an expression for k_2 near the LEEDS consensus expression (Fig. 4), which is considerably below the other high-temperature measurements.

A study of the ratio k_1/k_2 has been reported by Schott, Getzinger, and Seitz (SGS).¹⁴ Coupling k_1/k_2 (SGS) with k_1/k_3 from Ref. 11 and k_2/k_8 from this work, and using k_1 from GBO, gives k_8 (SGS) = $1.2 \times 10^{14} \exp(-34 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (cf. Fig. 5). The resulting calculated R values are the same as those of the solid curve in Fig. 1 above 1500 K and are somewhat higher than the solid curve below 1500 K, reflecting the fact that k_2

(SGS) is about 30% higher at those temperatures than the expression derived by us from Ref. 5. It can be seen from this result, as well as from Fig. 2, that the R values should yield k_2 below 1500 K with little dependence on the expressions used for other rate constants, provided that experimental difficulties (*vide infra*) can be overcome. Such a determination would allow k_8 to be directly obtained from the high-temperature data and would test the reliability of expressions for $k_2 k_3$ obtained from exponential growth constant data.

The choice of flow model assumed for calculations is known to have a considerable effect upon the determination of chain branching rate constants from exponential growth data.¹⁵ R values calculated using the rate constant set of Table I, assuming first ideal one-dimensional steady shock flow and then Mirels's limiting flow equations for turbulent boundary layers,¹² are compared to the laminar boundary layer calculations in Fig. 3. The flow model assumption has little effect on calculated R values above 1500 K, but there is a significant effect below that temperature. The determination of k_8 is thus not significantly sensitive to boundary layer assumptions.

IV. DISCUSSION

We cannot account for the large degree of scatter in the data at lower temperatures or the apparent failure of the calculations to match the sharp downward trend in most of the experimental R values below 1500 K. The calculated R values are significantly altered only by an unreasonable change in at least one of the rate constant expressions (cf. Fig. 2). Calculation of the Chapman-Jouguet velocity for the mixture showed that longitudinal instability¹⁶ of the shock wave was not a problem above 1100 K, but comparison of experimental induction times to the width of the shock tube indicated that transverse instability¹⁷ could have occurred at about 1400 K. Other possible causes of the low-temperature data scatter might be discontinuities due to transitions to turbulent boundary layers, or flow instabilities caused by mechanical nonidealities such as uneven or slow diaphragm rupture.¹⁸ The last possibility is a strong one, since recent studies in this laboratory have shown that poor diaphragm rupture is a relatively frequent occurrence under the operating conditions used for GMRT's low-temperature experiments.

Other possible difficulties with the experiments are evident on close inspection of Fig. 1. It can be seen that runs where He:Kr was used as a diluent appear to give R values slightly higher than average, while runs where the experimental gas was passed through a cold trap before admission to the experimental section appear to give uniformly lower R values than runs where this procedure was not used. The implications of the former are not clear, since too few of the He:Kr runs were considered to be acceptable data, but it can be tentatively concluded from the latter that trace impurities in the experimental gas may have a small but noticeable effect on the experimental R values.

None of the foregoing difficulties with the measurements alter the fact that our results show that the mag-

nitude of k_8 is considerably greater than a linear Arrhenius extrapolation of the AHW and room temperature results would indicate (cf. the LEEDS consensus, Fig. 5). Likewise, the temperature dependence we derive is greater than such an extrapolation would imply. Thus, the activation energy found by us is much higher than has been assumed in the past. In a 1961 review article, Voevodsky and Kondratiev¹⁹ mentioned $E_8 = 75$ kJ, from preliminary work by Azatyan. Kaufman and Del Greco²⁰ used this result along with their room temperature measurements to deduce an expression for k_8 with $E_8 = 4$ kJ. This expression was generally used until recent work by AHW¹³ on Reaction (–8) up to 1000 K gave $E_8 = 1.2$ kJ. In the high-temperature regime, Brokaw²¹ estimated that k_8 at 1600 K had to be considerably higher than expected to account for some of the experimental observations of Sulzmann *et al.*²² Since there is no experimental or theoretical justification for an assumption that k_8 expressions determined at shock tube temperatures can be linearly extrapolated on a $\log k$ vs $1/T$ plot to agree with k_8 values determined below 1000 K, or vice versa, the present result is not in disaccord with previous results.

Our experimental results having indicated that a linear Arrhenius graph does not describe the temperature dependence of Reaction (8), we fitted the data to an expression of the more general form $\log k = \log A + n \log T + E_A/RT$. This was done by a least-squares analysis in the $\log k$, $1/T$ plane. The two alternate expressions we obtained and the results of Refs. 13 and 23 were taken with equal weights. The resulting expressions $k = 1.68 \times 10^6 T^{2.03} \exp(4.99 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is shown in Fig. 5. Constraining the activation energy to be zero in a nonlinear least-squares analysis, again in the $\log k$, $1/T$ plane, gave $k = 10^{9.33} T^{1.11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is also shown in Fig. 5.

One interpretation of the nonlinear behavior of the k_8 and k_2 Arrhenius graphs is that the slope of the curves represents an "activation" energy which happens to be temperature-dependent. This was essentially the basis for an activated complex theory recently proposed²⁴ for the reaction



Another possible interpretation is that at elevated temperatures, these reactions may proceed predominantly through excited vibrational states of one or both reactant molecules,²⁵ an idea that will be pursued further in a forthcoming paper on the high-temperature rate of Reaction (9). Reactions (2), (8), and (9) are not the only reactions whose high-temperature rate constants do not agree with linear Arrhenius extrapolations from low temperature results. Nonlinearity in the plots of k_1 ^{5,26} and k_3 ¹¹ have also been noted. As additional information on other systems begins to approach the detailed understanding that has been achieved for the hydrogen-oxygen system, it is to be expected that more nonlinear Arrhenius graphs of this kind will appear.

V. CONCLUSIONS

Data on [OH] spikes in fuel-lean H_2 - O_2 -Ar mixtures

has been reanalyzed. By a systematic procedure that constrained the results to be compatible with other experimental data, a rate constant expression for Reaction (8) was deduced. The results of the analysis support (1) that the procedure of extrapolating low-temperature rate constant expressions to high temperatures on a linear plot of $\log k$ vs $1/T$ is not generally valid, and (2) that theoretical studies should be undertaken to explain the observed changes with increasing temperatures in the apparent activation energy of bimolecular reactions.

ACKNOWLEDGMENTS

This work was supported by the U. S. Army Research Office-Durham and the Robert A. Welch Foundation. We wish to acknowledge the participation of J. H. Owen and W. G. Mallard in many helpful discussions.

- ¹G. L. Schott and R. W. Getzinger, "Shock Tube Studies of the Hydrogen-Oxygen Reaction," in *Physical Chemistry of Fast Reactions*, edited by B. P. Levitt (Plenum, London, 1973), Vol. 1, p. 81.
- ²C. B. Wakefield, dissertation, The University of Texas, 1969.
- ³T. A. Brabbs, F. E. Belles, and R. S. Brokaw, Symp. Combust. 13th, Salt Lake City, UT, 1970, (1971), p. 129.
- ⁴C. J. Jachimowski and W. M. Houghton, *Combust. Flame* **15**, 125 (1970); **17**, 25 (1971).
- ⁵G. L. Schott, Symp. Combust. 12th, Poitiers, France, 1968 (1969), p. 569.
- ⁶R. W. Getzinger, L. S. Blair, and D. B. Olson, *Proceedings of the Seventh International Shock Tube Symposium*, edited by I. I. Glass (University of Toronto Press, Toronto, 1970), p. 605.
- ⁷W. G. Browne, D. R. White, and G. R. Smookler, Symp. Combust. 12th, Poitiers, France, 1968 (1969), p. 557.
- ⁸H. Henrici and S. H. Bauer, *J. Chem. Phys.* **50**, 1333 (1969).
- ⁹W. C. Gardiner, Jr., K. Morinaga, D. L. Ripley, and T. Takeyama, *J. Chem. Phys.* **48**, 1665 (1968). This work was preceded by theoretical prediction of spike behavior by C. W. Hamilton and G. L. Schott, Symp. Combust. 11th, Berkeley, CA, 1966 (1967), p. 635.
- ¹⁰G. L. Schott, *J. Chem. Phys.* **32**, 710 (1960).
- ¹¹W. C. Gardiner, Jr., W. G. Mallard, and J. H. Owen, *J. Chem. Phys.* **60**, 2290 (1974).
- ¹²H. Mirels, *AIAA J. (Am. Inst. Aeronaut. Astronaut.)* **2**, 84 (1963); *Phys. Fluids* **6**, 1201 (1963); **7**, 1208 (1964); **9**, 1265, 1907 (1966).
- ¹³E. A. Albers, K. Hoyermann, H. Gg. Wagner, and J. Wolf- rum, Symp. Combust. 13th, Salt Lake City, UT, 1970 (1971), p. 81.
- ¹⁴G. L. Schott, R. W. Getzinger, and W. A. Seitz, "Transient Oxygen Atom Yields in H_2 - O_2 Ignition and the Rate Coefficient for $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$," paper presented at the 164th National American Chemical Society Meeting, New York, August 1972; R. W. Getzinger, Symp. Combust. 14th, Pennsylvania State Univ., University Park, PA, 1972, (1973), 72.
- ¹⁵F. E. Belles and T. A. Brabbs, Symp. Combust. 13th, Salt Lake City, UT, 1970 (1971), p. 165, and in *Shock Tube Research: Proceedings of the Eighth Shock Tube Symposium*, p. 24, Chapman and Hall, 1971.
- ¹⁶R. A. Strehlow and A. Cohen, *Phys. Fluids* **5**, 97 (1962).
- ¹⁷R. A. Strehlow, 6th International Shock Tube Symposium, Ernst-Mach-Institut Bericht Nr. 4/68, p. 493, 1968; *Phys. Fluids* **12**, I-96 (1969).
- ¹⁸C. J. S. M. Simpson, T. R. D. Chandler, and K. B. Bridgman, *Phys. Fluids* **10**, 1894 (1967).

- ¹⁹V. V. Voevodsky and V. N. Kondratiev, *Prog. React. Kinet.* **1**, 41 (1961).
- ²⁰F. Kaufman and F. P. Del Greco, *Symp. Combust.* 9th, Ithaca, NY, 1962 (1963), p. 659.
- ²¹R. S. Brokaw, *Symp. Combust.* 11th, Berkeley, CA, 1966 (1967), p. 1063.
- ²²K. G. P. Sulzmann, B. F. Myers, and E. R. Bartle, *J. Chem. Phys.* **42**, 3696 (1965); **43**, 1220 (1965).
- ²³A. McKenzie, M. F. R. Mulcahy, and J. R. Steven, *J. Chem. Phys.* **59**, 3244 (1973).
- ²⁴F. Dryer, D. Naegeli, and I. Glassman, *Combust. Flame* **17**, 270 (1971); I. W. M. Smith and R. Zellner, *Chem. Soc. Faraday Trans. II*, **69**, 1617 (1973).
- ²⁵W. C. Gardiner, Jr., W. G. Mallard, M. McFarland, K. Morinaga, J. H. Owen, W. T. Rawlins, T. Takeyama, and B. F. Walker, *Symp. Combust.* 14th, Pennsylvania State Univ., University Park, PA, 1972 (1973), p. 61. The incorrect R formula given in the caption of Fig. 1 of this paper was not used in data reduction.
- ²⁶S. C. Kurzius and M. Boudart, *Combust. Flame* **12**, 477 (1968).
- ²⁷D. Gutman, E. A. Hardwidge, F. A. Dougherty, and R. W. Lutz, *J. Chem. Phys.* **47**, 4400 (1967).
- ²⁸D. Gutman and G. L. Schott, *J. Chem. Phys.* **46**, 4576 (1967).
- ²⁹C. J. Jachimowski and W. M. Houghton, *Combust. Flame* **15**, 125 (1970).
- ³⁰D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, "Critical Evaluation of Rate Data for Homogeneous, Gas-Phase Reactions of Interest in High-Temperature Systems," No. 2, Leeds Univ., 1968.
- ³¹J. E. Breen and G. P. Glass, *J. Chem. Phys.* **52**, 1082 (1970).
- ³²G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, *J. Chem. Phys.* **44**, 2877 (1966).
- ³³F. Kaufman, *Ann. Geophys.* **20**, 106 (1964).
- ³⁴D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions* (Butterworth, London, 1972), Vol. I, p. 119ff.
- ³⁵W. E. Wilson and J. T. O'Donovan, *J. Chem. Phys.* **43**, 1550 (1965).
- ³⁶A. A. Westenberg and N. deHaas, *J. Chem. Phys.* **58**, 4066 (1973).
- ³⁷M. F. R. Mulcahy and R. H. Smith, *J. Chem. Phys.* **54**, 5215 (1971).
- ³⁸G. A. Takacs and G. P. Glass, *J. Phys. Chem.* **77**, 1060 (1973).