

Rate constant of $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$ from 1350 to 1600 K

W. C. Gardiner Jr., W. G. Mallard, and J. H. Owen

Citation: *The Journal of Chemical Physics* **60**, 2290 (1974); doi: 10.1063/1.1681361

View online: <http://dx.doi.org/10.1063/1.1681361>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/60/6?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 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 constants for the reactions $\text{OH} + \text{H}_2\text{S} \rightarrow \text{H}_2\text{O} + \text{SH}$ and $\text{OH} + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_2$ over the temperature range 297–427°K

J. Chem. Phys. **64**, 3237 (1976); 10.1063/1.432663

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

J. Chem. Phys. **60**, 4676 (1974); 10.1063/1.1680967



Rate constant of $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$ from 1350 to 1600 K

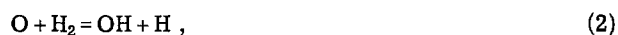
W. C. Gardiner, Jr., W. G. Mallard, and J. H. Owen

University of Texas at Austin, Austin, Texas 78712

(Received 19 November 1973)

Transient OH maxima were observed in the shock-initiated combustion of rich ($\text{H}_2:\text{O}_2:\text{Ar}=10:1:89$) hydrogen-oxygen-argon mixtures. Computer simulations of the reaction profiles were used to compare an assumed mechanism and set of rate constants with the experimental results. The expression $k_3=5.2\times 10^{13}\exp(-27\text{ kJ}/RT)\text{ cm}^3\text{ mol}^{-1}\cdot\text{s}^{-1}$ was derived for the reaction $\text{OH}+\text{H}_2=\text{H}_2\text{O}+\text{H}$ over the temperature range 1350–1600 K. The expression $k_3=10^{7.50T^{1.77}}\exp(-12.7\text{ kJ}/RT)\text{ cm}^3\text{ mol}^{-1}\cdot\text{s}^{-1}$ was derived combining our results with those of previous investigations spanning the temperature range 300–1800 K.

Shock tube experiments on the hydrogen-oxygen reaction in the high temperature-low pressure regime have proved to be fruitful in providing rate constant expressions for a number of elementary reactions.¹ One of the complicating features of this research has been the difficulty of separating the rate constant expressions for the branching reactions



This arises because the exponential growth constant governing the rate of chain center buildup during the induction period contains k_2 and k_3 only as their sum $k_s = k_2 + k_3$ and product $k_p = k_2k_3$, and because k_2 and k_3 turn out to have nearly the same values in the temperature range of most experiments.² It was pointed out by Hamilton and Schott³ that it would be possible to derive independent rate constant information on these reactions by following the concentration profiles of intermediates in the transition zone between the exponential growth zone and the recombination zone of the shock-initiated combustion of either very rich ($\text{H}_2:\text{O}_2$ ratio very large) or very lean ($\text{H}_2:\text{O}_2$ ratio very small) mixtures. From the previously observed absence of OH transients above the partial equilibrium level in the combustion of rich mixtures at pressures in the range 85–470 kPa, they were able to set an upper limit on the ratio of the rate constant for



to the rate constant for reaction (3) over the temperature range 1100–1900 K.

We discovered that small but distinct OH transients could be detected in rich mixtures shocked at starting pressures lower than in Hamilton and Schott's experiments if we used a Bi resonance lamp absorption source meticulously tuned to maximize the signal-to-noise ratio for the [OH] measurements. Extensive computer simulations using numerical integration of the rate equations for a large reaction mechanism confirmed their conclusion that the transients are primarily sensitive to the rate constant ratio k_1/k_3 . Using a k_1 expression from exponential growth constant measurements,⁴ the parameters of the transients were used to derive the expression $k_3=5.2\times 10^{13}\exp(-27\text{ kJ}/RT)\text{ cm}^3\text{ mol}^{-1}\cdot\text{s}^{-1}$.

Reference is made to a brief earlier account of the present results in a report describing, in a more gener-

al context, the use of post-induction period profiles for determination of elementary reaction rates.⁵

EXPERIMENTAL

The shock tube consisted of an experimental section made from 45×100 mm rectangular aluminum tube, 5.5 m long, with the observation ports located 4.0 m downstream from the diaphragm, and a 1.8 m long, 110 mm diameter cylindrical driver section connected to the experimental section by a tapered section 220 mm long. Two aluminum diaphragms, each of either 0.13 or 0.15 mm thickness, were used. They were impressed with a triangular petaling pattern and burst by evacuating the 50 mm long space between the two diaphragms. Hydrogen and hydrogen-nitrogen mixtures were used as drivers. Shock arrival was detected by 0.6 mm wide, 15 mm long tin resistance gauges deposited on Plexiglas mounts. A single gauge 50 mm upstream from the observation port was used to trigger the various electronic circuits, and a series of five gauges downstream from the observation port, spaced approximately 100 mm apart, was used for shock velocity measurements. The intergauge spacings were measured at the upstream edges of the tin strips using a horizontal cathetometer. The gauge signals were strongly amplified (typically 80 dB, 5 MHz bandwidth) and used to trigger a set of five high-speed comparators, which directed crystal-controlled 10 MHz clock signals to four three-digit decimal counting units. The system as a whole was found, by experiments in which the actual gauge signals were recorded together with the performance of the counters, to give true time intervals (typically ranging from 60 to 90 μs) to an accuracy of $\pm 0.1\text{ }\mu\text{s}$. It was generally found that the shock attenuation was about 2% per meter, and that smaller random variations at the 0.1–0.3 μs level were characteristic. The effects of this unsteady wave propagation on the present experiments are small enough to be disregarded; their effects on induction time measurements will be discussed in a later paper.

The spectroscopic observation ports were three polished quartz discs of 19 mm open diameter, located on opposite narrow sides and on the top of the tube. External slits 2 mm wide, 50 mm away from the port, defined the beam widths and resolution time. All ports and gauges were sized and shimmed to afford the least possible disturbance of the flow.

Concentration measurements of OH radical were made

with a Bi (306.7 nm) resonance source lamp spectrophotometric method.⁶ The lamps contained Bi metal chips in a short (about 800 mm) length of 8 mm diameter quartz tube containing about 2.7 kPa of helium buffer gas. They were driven by a 100 W, 2.45 GHz diathermy oscillator, appropriately modified to suppress line ripple, in an FEB Number 2a cavity.⁷ It was found that the signal-to-noise ratio of the OH observations could be substantially enhanced by judicious placement of the lamp in the cavity and by meticulous tuning, to the extent, in fact, that the observations reported here would have been impossible with absorption sources described before.¹ The 306.7 nm radiation was isolated from the rest of the lamp output by a filter consisting of a Corning 9863 glass plate 3 mm thick and a 6 mm path of NiSO_4 solution; this filter passed about 55% of the 306.7 line intensity and effectively nothing else from the lamp. The transmitted intensity was monitored by an S-13 photomultiplier and conventional electronics; conventional oscilloscope trace photography was used to record the absorption profiles. The oscilloscopes used were calibrated repeatedly both in time base and voltage sensitivity while these experiments were in progress.

Although chemiluminescence is weak in rich $\text{H}_2\text{-O}_2$ combustion, under the conditions of our experiments it

occurs as a short pulse just large enough to distort the transient OH absorption signals significantly. In order to compensate for this, a second photomultiplier-filter combination viewed from above the shock tube essentially the identical volume of reacting gas that the absorption beam viewed across the tube. Using rather stronger shock waves than in the rest of the experiments, the gain of the upper photomultiplier was adjusted until the pure chemiluminescence signals from both stations were identical. In absorption experiments, the upper photomultiplier signal was then subtracted electronically from the side photomultiplier signal to cancel the contribution of chemiluminescent emission from the latter.

Gas mixtures were prepared manometrically from commercial gases of the greatest stated purity available, without attempts at further purification. One mixture was purchased from a commercial supplier. Mass-spectrometric analysis showed it to be free of contamination over 5 ppm except for a trace of N_2 . The actual compositions were so close to the nominal $\text{H}_2:\text{O}_2:\text{Ar} = 10:1:89$ that the differences could be neglected. The shock tube itself had a leak and outgassing rate of about 4×10^{-4} Pa/s, which proved by RGA analysis to be entirely air and water. Prior to experiments the shock tube was usually pumped to about 1 mPa. All experi-

TABLE I. Rate constant expressions.

	Reaction		Rate constant ^a	Reference
01	$\text{H} + \text{H} + \text{M} = \text{H}_2 + \text{M}$	$\text{M} = \text{Ar}, \text{O}_2$	$k_{01} = 1.0 \times 10^{15}$	11
		$\text{M} = \text{H}_2$	$k_{01A} = 2.5 k_{01}$	b
		$\text{M} = \text{H}$	$k_{01B} = 20 k_{01}$	b
		$\text{M} = \text{H}_2\text{O}$	$k_{01C} = 6 k_{01}$	c
02	$\text{O}_2 + \text{M} = 2\text{O} + \text{M}$	$\text{M} = \text{Ar}, \text{H}_2$	$k_{02} = 1.85 \times 10^{11} T^{1/2} \exp(-400 \text{ kJ}/RT)$	d
		$\text{M} = \text{O}$	$k_{02A} = 30 k_{02}$	d
		$\text{M} = \text{O}_2$	$k_{02B} = 10 k_{02}$	d
03	$\text{H}_2 + \text{O}_2 = 2\text{OH}$		$k_{03} = 1.7 \times 10^{13} \exp(-200 \text{ kJ}/RT)$	e
1	$\text{H} + \text{O}_2 = \text{OH} + \text{O}$		$k_1 = 1.22 \times 10^{17} T^{-0.907} \exp(-69.58 \text{ kJ}/RT)$	4
2	$\text{O} + \text{H}_2 = \text{OH} + \text{H}$		$k_2 = 4.76 \times 10^{17} T^{-0.907} \exp(-69.58 \text{ kJ}/RT)$	10
3	$\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$		$k_3 = 5.2 \times 10^{13} \exp(-27 \text{ kJ}/RT)$	5
4	$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	$\text{M} \neq \text{H}_2\text{O}$	$k_4 = 2.0 \times 10^{15} \exp(3.6 \text{ kJ}/RT)$	f
		$\text{M} = \text{H}_2\text{O}$	$k_{4A} = 25 k_4$	f
5	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	$\text{M} \neq \text{H}_2\text{O}$	$k_5 = 7.5 \times 10^{23} T^{-2.6}$	g
		$\text{M} = \text{H}_2\text{O}$	$k_{5A} = 20 k_5$	g
6	$\text{HO}_2 + \text{H} = 2\text{OH}$		$k_6 = 6.0 \times 10^{13}$	h
7	$\text{HO}_2 + \text{O} = \text{OH} + \text{O}_2$		$k_7 = 1.0 \times 10^{13}$	h
8	$\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$		$k_8 = 5.5 \times 10^{13} \exp(-29 \text{ kJ}/RT)$	5
9	$\text{H}_2 + \text{HO}_2 = \text{H}_2\text{O} + \text{OH}$		$k_9 = 2.0 \times 10^{11} \exp(-100 \text{ kJ}/RT)$	i

^aConcentration units are mol cm⁻³.

^bT. A. Jacobs, R. R. Giedt, and N. Cohen, *J. Chem. Phys.* **47**, 54 (1967).

^cR. W. Getzinger and L. S. Blair, *Combust. Flame* **13**, 271 (1969); A. Gay and N. H. Pratt, *Shock Tube Research: Proceedings of the Eighth Shock Tube Symposium* (Chapman and Hall, London, 1971).

^dW. S. Watt and A. L. Myerson, *J. Chem. Phys.* **51**, 1639 (1969).

^eC. J. Jachimowski and W. M. Houghton, *Combust. Flame* **17**, 25 (1971).

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

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

^hW. G. Browne, D. R. White, and G. R. Smookler, *Symp. Combust.*, 12th, Poitiers, France, 1968 (1969), p. 557.

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

ments reported here were done with $P_1 = 2.67$ kPa, after preliminary runs showed that higher pressures gave absorbance signals that were too weak to be useful. Shocks were usually fired within 200 s of filling the experimental section.

All observations were made in incident shock waves. The flow parameters were calculated from the starting conditions in the conventional way, assuming vibrationally relaxed, chemically unreacted gas and JANAF thermochemical properties. All temperatures referred to in this paper are the no-reaction shock temperatures.

Comparison of observations with mechanistic assumptions was done by generating calculated OH profiles using numerical integration of the differential equations describing incident shock flow and the reaction mechanism given in Table I. The effect of boundary layer growth was taken into account by replacing the conventional constant-area, steady-flow conservation equations with the variable-area, steady-flow conservation equations appropriate for describing free-stream flow in the presence of a boundary layer growing in thickness with distance behind the shock front. Mirels'⁸ variable-area equations for laminar boundary layers at limiting separation were used, assuming the test gas to be pure argon. It was confirmed by monitoring the trigger heat-gauge signal that the boundary layer remained laminar throughout the hot flow. Limiting separation was of course not achieved in these experiments. Nonetheless, Mirels' formulas for l_m were used on the assumption that they would give a description of the free-stream flow that would take sufficiently accurate account of boundary layer growth for present purposes. Subsequent analysis of the steady-flow free-stream conditions supported this assumption.⁹ In trial profile calculations, it was found that the results of present interest are not sensitive to the value chosen for l_m , within reasonable limits. Indeed, it was found that using Mirels' turbu-

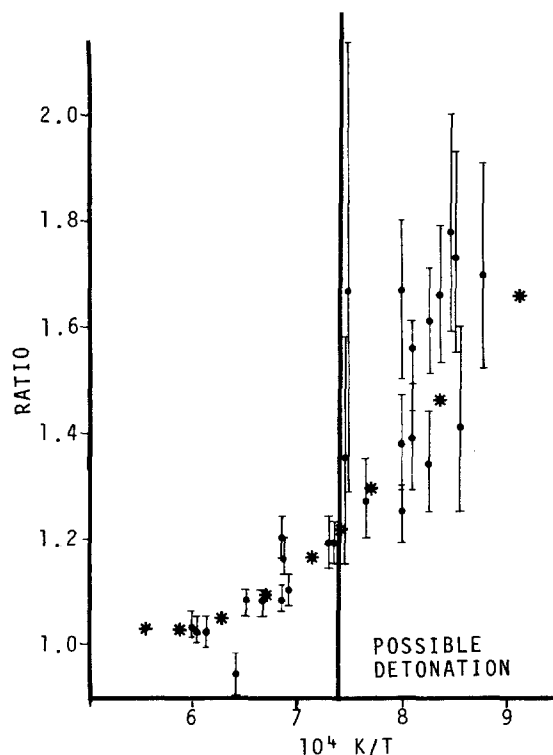


FIG. 2. Experimental and computed peak ratios. The asterisks represent R values calculated using the set of rate constant expressions shown in Table I. The error bars on the data represent 1.0 mV error in reading the oscilloscope trace photographs.

lent flow model caused almost no change in the calculated results, nor did the use of a locally similar flow model that allowed for gas composition and directly calculated the boundary layer properties from viscosity considerations. There was, however, a significant difference between the results assuming variable area flow and those assuming constant area flow.

RESULTS

Tracings of oscilloscope records of the emission-corrected transmitted intensity for runs spanning the temperature range 1200–1540 K are shown in Fig. 1. The expected appearances of OH absorption, after an induction period, are seen to be followed, for the lower-temperature runs, by small transient maxima before the gradual decay to equilibrium begins. The smooth character of the profiles at the maximum made it somewhat awkward to describe this in a way that can be directly correlated with the rates of specific elementary reactions. We chose to parametrize the maximum of each experimental record as follows. The transmitted intensities 100 and 200 μs after the maximum were taken as tie points for a straight-line back extrapolation of the slow decay due to recombination. The vertical distance between the maximum intensity and the preshock intensity I_0 is defined as I_M ; the vertical distance between the back extrapolation line and the preshock intensity, again at the time of the maximum absorption, is defined as I_B . If Beer's Law is valid for these observations, we can identify the magnitude of the excursion of the OH

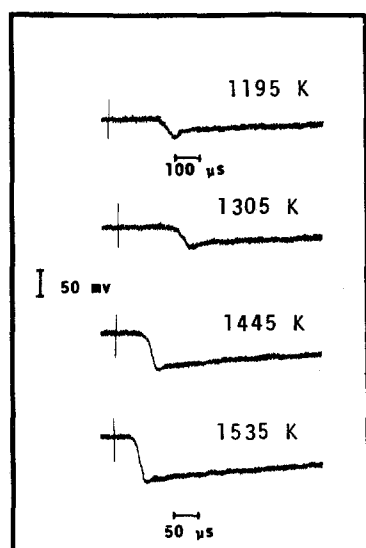


FIG. 1. Sample experimental records. The traces at no-reaction shock temperatures 1195 and 1305 K are below the detonation limit defined by the Chapman-Jouguet condition. Shock arrival is denoted by the vertical bars.

concentration during the maximum as $[\text{OH}]_{\text{max}}/[\text{OH}]_{\text{back-extrapolated}}$ and assign to it the experimental parameter $R = \ln(1 - I_M/I_0)/\ln(1 - I_B/I_0)$. A parameter of secondary usefulness is the duration of the maximum D , taken as the width of the profile halfway between the back extrapolation and the maximum levels (cf. Fig. 1).

Values of R and D are plotted versus inverse temperature in Figs. 2 and 3. The error bars on R represent the consequences of assuming a reading error of ± 1 mV on the oscilloscope traces. The error bar on D corresponds to ± 5 μs or ± 1 mm of oscilloscope trace. That these estimates are generous can be seen by comparing the records in Fig. 1 with their entries in Figs. 2 and 3. Also indicated on Figs. 2 and 3 is the no-reaction shock temperature corresponding to a steady one-dimensional detonation wave for this experimental mixture, as given by the Chapman-Jouguet condition.

The sensitivity of the experimental values of R and D to assumed rate constants was investigated by extracting R and D values from numerical integrations using various assumed sets of rate constant expressions. The sensitivities that obtain for halving and doubling the pertinent rate constants from the set of rate constant expressions that was finally taken to represent the data are displayed in Figs. 4 and 5.

DISCUSSION

The small size and signal-to-noise ratio of the observed transients mean that the parameters must be quite sensitive to specific aspects of the reaction kinetics in order for meaningful deductions to be possible. Fortunately, this specific sensitivity exists. It may be seen in Fig. 4 that reactions (1) and (3) are by far the most important contributors to determining the parameter R ; recombination reactions exert small but perceptible influences, and other reactions are of no importance. The effect of using ideal (constant-area) flow in-

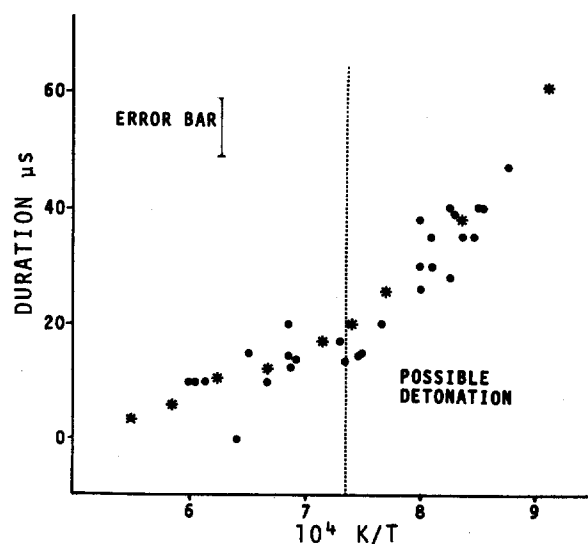


FIG. 3. Durations. The asterisks represent D values calculated using the set of rate constant expressions in Table I. The error bars represent ± 5 μs . All points at $T < 1350$ are in the detonation region (to right of dotted line).

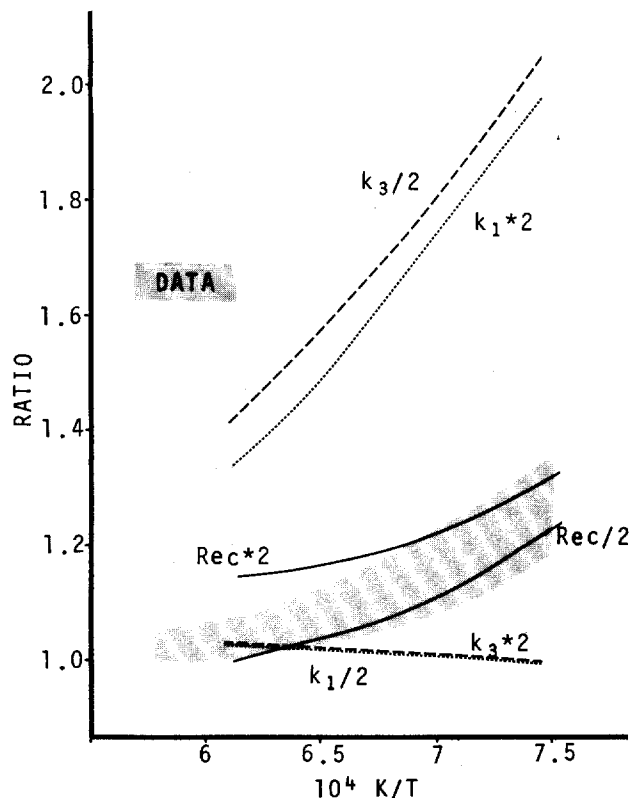


FIG. 4. Sensitivity of R values to rate constant expressions. The gray area represents the maximum extent of the data scatter (cf. Fig. 2). Rec refers to the $\text{H} + \text{H} + \text{M}$ recombination reaction. No other rate constant doublings or halvings produced a calculated line outside the data scatter area.

stead of boundary layer corrected flow is small and falls within the data scatter. The D parameter, on the other hand, proved to be relatively unspecific and insensitive, and is only suitable for a final consistency check. The effects of reactions (1) and (3) are essentially reciprocal, confirming Hamilton and Schott's original proposal that the ratio k_1/k_3 critically determines R .

If this were the first high temperature study of the kinetics of the $\text{H}_2\text{-O}_2$ reaction, the present results would merely be an indication of a rate constant ratio based on an assumed mechanism. Since extensive research has already been done, however, these results are amenable to quite specific interpretation. In the first place, the mechanism described in Table I is now rather well understood to be complete for the range of experimental conditions we investigated. Secondly, there is already sufficient rate constant information on k_1 , k_2 , and the recombination reactions to permit the R parameter to be used as a measure of k_3 alone.

The most direct measurement of the critical rate constant k_1 is from exponential growth constants; the results of several independent investigations are in remarkably close accord with one another, and in good accord with the results of other types of experiments.¹ Of the various k_1 expressions available, we chose Schott's^{2,4} for a reference value. Schott, Getzinger, and Seitz's expression for k_2 was used.¹⁰ Finally, we chose recombination rate constants consistent with the long-term de-

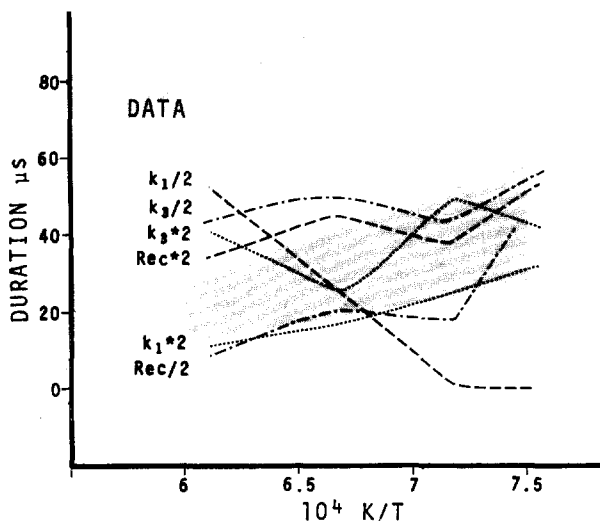


FIG. 5. Sensitivity of D values of rate constant expressions. It can be seen that D values do not provide a guideline to adjustment of rate constant expressions.

cay of OH radical concentration in these experiments.¹¹ These rates are generally within a factor of 2 of other reported rates for recombination.

With these assumed expressions for all the pertinent rate constants but k_3 , numerical integrations for various k_3 values were done until the R data were well fitted, as shown in Fig. 2, with $k_3 = 5.2 \times 10^{13} \exp(-27 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \cdot \text{s}^{-1}$. As shown in Fig. 3, the same k_3 expression is in good accord with the D data. In Fig. 6, it is compared with various previously proposed k_3 expressions.

The sensitivity graphs of Figs. 4 and 5 were then constructed using halved and doubled values of the rate constants that have perceptible influences upon R and D .

Our expression for k_3 is dependent on chemical kinetics and gas dynamics assumptions. The former are subject to facile modification through Fig. 4, should any of the assumed rate constant expressions later prove to be seriously in error. The assumption that Mirels' formulas for limiting laminar boundary layer flow are sufficiently accurate descriptions of the free-stream shocked gas flow in these experiments will be discussed at length in a forthcoming paper on induction times, in which connection the gas dynamics assumptions play a more critical role.

It is to be noted that the present k_3 results, when examined together with other results on an Arrhenius presentation such as in Fig. 6, indicate the presence of a distinct upwards curvature from a consensus straight line through data taken at lower temperatures. In order to provide a quantitative expression for this curvature, a democratic nonlinear least-squares fit to all of the data shown in Fig. 6 was found. This was done in the $\log k_3$, $1/T$ plane assuming the functional form $\log k_3 = A + B \log T + C/T$. Each investigation was assigned equal total weight in the least-squares analysis. Where a single rate constant value was reported, it was assigned

weight of unity; where an expression was reported, the values at the highest and lowest temperatures were used in the analysis with weight one-half each; where a number of data points were reported, they were all used, with weights equal to the inverse of the total number of data points reported in that investigation. The resulting nonlinear rate constant expression $k_3 = 10^{7.50} T^{1.77} \exp(-12.7 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \cdot \text{s}^{-1}$ is shown in Fig. 6. It is noteworthy that an error band of a factor of 2 width would enclose all of the experimental data except for the highest temperature points of two of the flame structure studies. The difference between the nonlinear and the linear consensus fits to the data is seen to be signifi-

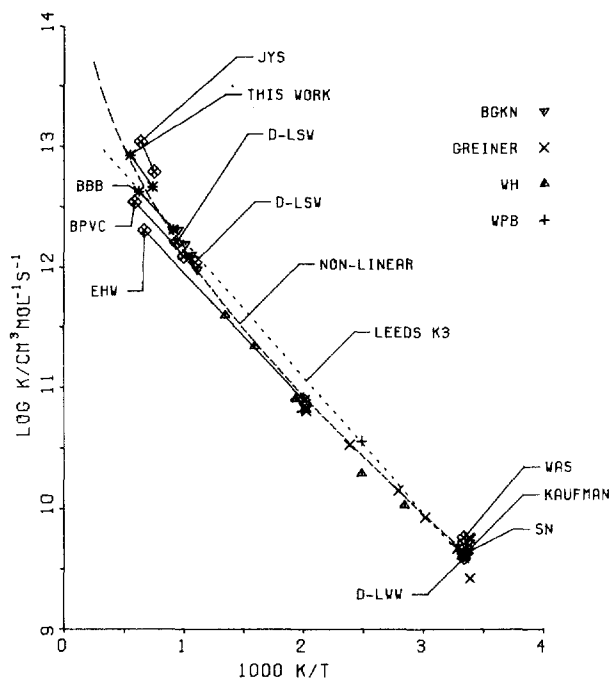


FIG. 6. Arrhenius graph for $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$. The symbols refer to literature sources of experimental values as follows: BBB, Ref. 14; BGKN, Ref. 15; BPVC, Ref. 16; D-LSV (upper): Ref. 17; D-LSV (lower): Ref. 18; D-LWW: Ref. 19; EHW: Ref. 20; GREINER: Ref. 21; JYS: Ref. 22; KAUFMAN: Ref. 23; SN: Ref. 24; WAS: Ref. 25; WH: Ref. 12; WPB: Ref. 26. The dotted straight line LEEDS K3 is a consensus expression recommended by D. 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*, Leeds U. P., 1968; a later review is given by D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions* (Butterworths, London, 1972), Vol. I, p. 77 ff. The dashed line NON-LINEAR is a least-squares fit to all the experimental data shown. The weight assigned to each point is the inverse of the number of data points reported in each paper; for papers reporting a k_3 expression rather than k_3 values, k_3 values were calculated at the upper and lower temperature limits of the investigation, and each was assigned the weight $\frac{1}{2}$. The BBB expression was actually obtained from an average of 26 data points scattered over about $0.7 \log k_3$ units, near $1000/T = 0.8$, together with the D-LWW room temperature value. The EHW expression is a fit to 12 data points from two flames spanning the temperature range 476–1495 K. The five data points from their hotter flame (1150–1495 K) are scattered among the lower BBB points, and are all definitely below the BPVC expression.

cant.

Theoretical interpretation of the deviation from linearity observed here can readily be done in the activated complex theory or collision theory frameworks. It has already been noted that the simplest possible activated complex theory model is not successful for this reaction,¹² while parametric variations without regard for the model complex can lead to adequate reproduction of the observed curvature.¹³ An extensive discussion of applications of both activated complex theory and collision theory to the Arrhenius graph curvature for this reaction will be presented at a later date.

ACKNOWLEDGMENTS

This research was supported by the U.S. Army Research Office, Durham and the Robert A. Welch Foundation.

- ¹G. L. Schott and R. W. Getzinger, in *Physical Chemistry of Fast Reactions*, edited by P. B. Levitt (Plenum, London, 1973), Vol. I.
- ²G. L. Schott, Symp. Combust., 12th, Poitiers, France, 1968 (1969), p. 129.
- ³C. W. Hamilton and G. L. Schott, Symp. Combust., 11th, Berkeley, 1966 (1967), p. 635.
- ⁴G. L. Schott, Combust. Flame **21**, 357 (1973).
- ⁵W. 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., 1972 (1973), p. 61.
- ⁶D. L. Ripley, dissertation, University of Texas, Austin, TX, 1967.
- ⁷F. C. Fehsenfeld, K. M. Evenson, and H. P. Broida, Rev. Sci. Instrum. **36**, 294 (1965).
- ⁸H. Mirels, AIAA J. **2**, 84 (1963); Phys. Fluids **6**, 1201 (1963); **7**, 1208 (1964); **9**, 1265, 1907 (1966).
- ⁹E. S. Ehrhardt, thesis, University of Texas, Austin, TX, 1973.
- ¹⁰G. L. Schott, R. W. Getzinger, and W. A. Seitz, "Transient Oxygen Atom Yields in $\text{H}_2\text{-O}_2$ 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., 1972 (1973), p. 72.
- ¹¹W. G. Mallard and J. H. Owen, Int. J. Chem. Kin. (to be published).
- ¹²A. A. Westenberg and N. deHaas, J. Chem. Phys. **58**, 4061 (1973).
- ¹³Compare discussion comments following Ref. 5.
- ¹⁴T. A. Brabbs, F. E. Belles, and R. S. Brokaw, Symp. Combust., 13th, Salt Lake City, 1970 (1971), p. 129.
- ¹⁵V. P. Balakhnin, Yu. N. Gershenzon, V. N. Kondratiev, and A. B. Nalbandyan, Dokl. Akad. Nauk SSSR **170**, 1117 (1966).
- ¹⁶W. G. Browne, R. P. Porter, J. D. Verlin, and A. H. Clark, Symp. Combust., 12th, Poitiers, France, 1968 (1969), p. 1035.
- ¹⁷G. Dixon-Lewis, M. M. Sutton, and A. Williams, J. Chem. Soc. 1965, 5724.
- ¹⁸G. Dixon-Lewis, M. M. Sutton, and A. Williams, Symp. Combust., 10th, Univ. Cambridge, Engl., 1964 (1965), p. 495.
- ¹⁹G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, J. Chem. Phys. **44**, 2877 (1966).
- ²⁰K. H. Eberius, K. Hoyer mann, and H. Gg. Wagner, Symp. Combust., 13th, Salt Lake City, 1970 (1971), p. 713.
- ²¹N. R. Greiner, J. Chem. Phys. **51**, 5049 (1969).
- ²²D. R. Jenkins, V. Yumlu, and D. B. Spalding, Symp. Combust., 11th, Berkeley, 1966 (1967), p. 779.
- ²³F. Kaufman, Ann. Geophys. **20**, 106 (1964).
- ²⁴F. Stuhl and H. Niki, J. Chem. Phys. **57**, 3671 (1972).
- ²⁵H. Wise, C. M. Ablow, and K. M. Sancier, J. Chem. Phys. **41**, 3569 (1964).
- ²⁶E. L. Wong, A. E. Potter, and F. E. Belles, NASA TN D-4162 (1967), and NASA TN D-5707 (1970).