Shock Tube and Modeling Study of the $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ Reaction over a Wide Range of Composition, Pressure, and Temperature

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The rate coefficient of the reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ (1) was determined using OH laser absorption spectroscopy behind reflected shock waves over the temperature range 1050–2500 K and the pressure range 0.7–4.0 atm. Eight mixtures and three stoichiometries were used. Two distinct and independent criteria were employed in the evaluation of $k_1$. Our recommended expression for $k_1$ is $k_1 = 7.13 \times 10^{13} \exp(-6957 \text{K/T}) \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ with a statistical uncertainty of 6%. A critical review of recent evaluations of $k_1$ yields a consensus expression given by $k_1 = 7.82 \times 10^{13} \exp(-7105 \text{K/T}) \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ over the temperature range 960–5300 K. We do not support a non-Arrhenius rate coefficient expression, nor do we find evidence of composition dependence upon the determination of $k_1$.

Introduction

The reaction between hydrogen atom and oxygen molecule,

$$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \quad (\Delta H_{298}^o = 70.2 \text{ kJ mol}^{-1}) \quad (1)$$

is the main chain branching reaction in the oxidation of hydrogen- and hydrocarbon-based fuels. About 80% of the oxygen in a typical atmospheric pressure hydrocarbon flame is consumed by this reaction. That this reaction is rate controlling is due to its high endothermicity. Thus, ignition delays and flame speeds, important and easily measurable combustion characteristics, are often found to be sensitive to the rate coefficient of this reaction.

The central role of reaction 1 in combustion chemistry has made it the object of intense scrutiny. In 1972, Baulch et al. (BDHL) reviewed the available data and recommended the rate coefficient expression $k_1 = 2.2 \times 10^{14} \exp(-8450 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. They argued that the activation energy should not be less than the endothermicity based upon the bimolecular nature of the reaction and their expectation of a nonnegative activation energy of the reverse reaction (which was subsequently found to be negative). In 1973, Schott measured the exponential growth rate of CO$_2$ chemiluminescence in shock-heated H$_2$/CO/O$_2$/Ar mixtures and reported a rate coefficient expression with a temperature-dependent preexponential factor,

$$k_1 = 1.22 \times 10^{17} \exp(-8369 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}. \quad (2)$$

For over a decade these two expressions formed the upper, BDHL, and lower, Schott, accepted limits for $k_1$. Schott suggested that this may be due not to differences in experimental techniques and data reduction methodologies but rather to differences in the reactant partial pressures used in the various studies, i.e., a composition effect. In this study we performed a series of experiments over a wide range of composition and pressure to explore the effect, if any, of reactant partial pressure upon the determination of $k_1$.

Experimental Section

Shock Tube System. The experimental setup is shown in Figure 1. Experiments were performed in a rolled square stainless steel shock tube 63.5 mm in cross section. Shocks were initiated by bursting an aluminum diaphragm with a cross-shaped knife-edge plunger. The test section was routinely pumped between experiments to $3 \times 10^{-6}$ Torr using a Varian Turbo-V60 turbopump. A combined leak and outgassing rate of 5 $\times 10^{-6}$ Torr min$^{-1}$ was measured. To further alleviate contamination, neither the driven nor driver sections was rough pumped below 500 mTorr. The gas handling system was constructed using Varian high-vacuum valves and fittings. Test gas pressures were measured using a Druck Model DPI-260 pressure transducer.

Two 25.4 mm diameter S1-UVA quartz windows, centered 12.7 mm from the end plate, were flush mounted with the shock tube inner walls. Shock passage was detected using four $113A21$ PCB Piezotronics pressure transducers flush mounted with the shock tube inner wall, one of which was mounted at the axial position of the window center line. Shock temperatures between each transducer pair were measured and fitted to a second-order polynomial in distance that was then used to obtain the extrapolated shock temperature at the end plate. Shock velocities were computed using this velocity and standard methods assuming full vibrational relaxation and no chemical reaction at the shock front. NASA thermochemical data were used to predict the experimental value now being a factor of 1.7 higher at 2000 K. This prompted a flurry of experimental and theoretical investigations of the title reaction using more advanced diagnostics and techniques.

Even though numerous experimental studies have been performed, disagreement still exists among the reported values of $k_1$. Schott has suggested that this may be due to differences in experimental techniques and data reduction methodologies rather than differences in the reactant partial pressures used in the various studies, i.e., a composition effect. In this study we performed a series of experiments over a wide range of composition and pressure to explore the effect, if any, of reactant partial pressure upon the determination of $k_1$. **Abstract published in Advance ACS Abstracts, August 15, 1995.**
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Figure 1. Schematic diagram of the experimental apparatus. The probe laser beam path is offset for clarity of presentation.

used throughout the calculations. Computed shock properties were corrected for effects due to the interaction between the reflected shock front and the boundary layer following the adiabatic equation of state method described by Michael and Sutherland. The postshock pressure, needed for the boundary layer correction, was measured using the pressure transducer centered above the windows. The initial test gas pressure was added to this pressure.

The temporal profile of OH concentration was monitored using the P$_2$(9) line of the (0,0) band of the A$^2\Sigma^+ \rightarrow \chi^2\Pi$ transition at 310.032 nm (air). A Coherent CR-699-21 ring-dye laser running Krypton Red dye was pumped by a Coherent Innova 200 argon ion laser. Dye solution temperature was maintained at 278 K to give optimum laser performance. Intracavity doubling via an angle-tuned LiIO$_3$ crystal produced a single-mode 5 mW UV beam with a 2 mm beam diameter. Center wavelength of the OH absorption line was determined by passing part of the UV beam through a burner-stabilized CH$_4$/air flame. The lasers, optical components, and the detection system described below were mounted on a pneumatically stabilized Newport MST series optical table.

Optical Detection System. A double-beam scheme was employed for signal detection. The UV beam was split into two beams. The first beam was directed through the shock tube at the center of the windows. If the expected absorbance for an experiment was small, the beam was reflected back through the shock tube at the same streamwise distance but vertically displaced from the incoming beam and onto the detector, i.e., double pass. For experiments with larger expected absorbance, the beam was returned to the detector after being steered around the shock tube, i.e., single pass. An iris was set in front of the detector both to limit the spurious signal due to hot gas emission from within the shock tube and to help establish "time zero", taken as the center of the schlieren signal caused by shock passage. The second beam was split again, and one part was directed to a reference detector and the other directed through a CH$_4$/air flame and onto a third detector. All three detectors were THORN EMI Model 9224QB photomultiplier tubes (PMT) using a five-dynode configuration to ensure optimum linearity. High-speed buffer/amplifiers were used to isolate the anodes. An overall electronic time constant of 0.2 ms was determined for the PMT/electronics/cable system. Background light reduction was achieved by mounting a narrow-band interference filter in front of each PMT. The reference, probe, difference (probe dc − reference ac), and the last pressure transducer signals were recorded on a four-channel Nicolet 4094C digital oscilloscope.

Figure 2. Typical experimental records. (a, top) 2.0% H$_2$, 0.5% O$_2$, 97.5% Ar, $T_s = 1556$ K, and $P_s = 0.75$ atm; (b, bottom) 2.0% H$_2$, 0.2% O$_2$, 97.8% Ar, $T_s = 2163$ K, and $P_s = 1.99$ atm. Spikes at time zero are schlieren signals due to reflected shock front passage. Smooth lines are computed OH absorption profiles using the Table 2 mechanism and the OH absorption coefficients determined from $A_{\text{max}}$.

with Nicolet 4570 plug-in units. The pressure signal served as the trigger source for the oscilloscope. Reaction progress was followed using the difference signal. Further details of the experimental apparatus are given in ref 11.

Test Gas Mixtures. The test gas mixtures were prepared manometrically and allowed to stand for 48 h before use. The maximum uncertainty of the reactant concentration was 0.5% or less for each component. Gases were used as delivered with no further purification. Stated purities of the gases were as follows: H$_2$, 99.9995% (Linde Research Grade, THC as CH$_4$ <0.3 ppm); O$_2$, 99.6% (Linde Zero Grade, THC as CH$_4$ <0.3 ppm); Ar, 99.996% (Linde Zero Grade, THC as CH$_4$ <0.3 ppm). These purity levels were confirmed by gas chromatographic analysis with flame ionization detection.

Results

Typical transmission profiles at different experimental conditions are shown in Figure 2. After an induction period light absorption increases rapidly due to the essentially exponential growth of OH concentration caused by chain branching and propagation reactions. All experiments show rapid achievement of an OH super-equilibrium concentration followed by a slow relaxation to equilibrium at long times.

Data reduction was accomplished using a small set of relevant information derived from the absorption traces, namely, $A_{\text{max}} = (1 - I/I_0)_{\text{max}}$, $N_{\text{S}} = -d(I/I_0)/dt|_{t=0}$, and one characteristic time, $t_0$, the time at which the absorbed light intensity has reached 50% of $A_{\text{max}}$. These three observables were chosen based upon sensitivity analysis using a trial $\text{H}_2/\text{O}_2$ reaction mechanism. It has been shown previously that a small number of appropriately chosen observables can embody the full information content of an experiment.

Experimental conditions, measured observables, and determined $k_i$ values are given in Table 1. Eight rich mixtures of equivalence ratios of 2, 5, and 10 were used. Mixture compositions were selected such that maximum absorption was less than 0.55 for all conditions. Reflected shock temperatures and pressures ranged from 1050 to 2500 K and from 0.7 to 4.0 atm, respectively. Temperatures obtained using the boundary layer correction were always higher than the ideal shock temperatures, on average by 1.4%. A clear dependence of the
### Table 1: Experimental Conditions and Results

<table>
<thead>
<tr>
<th>$T_s$</th>
<th>$P_s$</th>
<th>$A_{max}$</th>
<th>$NS_{max}$</th>
<th>$t_{50}$</th>
<th>$k_t^{1/102}$</th>
<th>$T_s$</th>
<th>$P_s$</th>
<th>$A_{max}$</th>
<th>$NS_{max}$</th>
<th>$t_{50}$</th>
<th>$k_t^{1/102}$</th>
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<td>15.706</td>
<td>618.0</td>
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<td>1102</td>
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<td>0.334</td>
<td>15.706</td>
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<td>0.334</td>
<td>15.706</td>
<td>618.0</td>
<td>0.092</td>
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</table>

#### Conditions and Results

- **0.4% H$_2$, 0.1% O$_2$, 99.5% Ar (\(\phi = 2\))**
  - 1052: 2.289, 0.334, 15.706, 618.0, 0.092, 1102, 2.289, 0.334, 15.706, 618.0, 0.092
  - 1074: 0.964, 0.303, 7.293, 1005.0, 0.104, 1115, 2.289, 0.334, 15.706, 618.0, 0.092
  - 1086: 0.940, 0.294, 6.642, 958.5, 0.112, 2628, 2.289, 0.334, 15.706, 618.0, 0.092

- **0.4% H$_2$, 0.1% O$_2$, 99.5% Ar (\(\phi = 2\))**
  - 1234: 0.945, 0.294, 6.642, 958.5, 0.112, 2628, 2.289, 0.334, 15.706, 618.0, 0.092

- **0.4% H$_2$, 0.1% O$_2$, 99.5% Ar (\(\phi = 2\))**
  - 1357: 0.771, 0.356, 7.162, 612.0, 0.420, 1808.0, 0.846, 0.409, 1816.0, 161.5

- **0.4% H$_2$, 0.1% O$_2$, 99.5% Ar (\(\phi = 2\))**
  - 1337: 0.796, 0.351, 7.162, 612.0, 0.420, 1808.0, 0.846, 0.409, 1816.0, 161.5

- **0.4% H$_2$, 0.1% O$_2$, 99.5% Ar (\(\phi = 2\))**
  - 1422: 0.859, 0.437, 10.011, 384.0, 0.601, 2017.0, 0.577, 0.429, 2140.0, 128.0

- **0.4% H$_2$, 0.1% O$_2$, 99.5% Ar (\(\phi = 2\))**
  - 1754: 0.702, 0.353, 7.183, 612.0, 0.420, 1808.0, 0.846, 0.409, 1816.0, 161.5

- **0.4% H$_2$, 0.1% O$_2$, 99.5% Ar (\(\phi = 2\))**
  - 1837: 0.771, 0.356, 7.162, 612.0, 0.420, 1808.0, 0.846, 0.409, 1816.0, 161.5

- **0.4% H$_2$, 0.1% O$_2$, 99.5% Ar (\(\phi = 2\))**
  - 1959: 0.733, 0.445, 10.885, 343.0, 0.837, 2136.0, 0.851, 0.487, 2473.0, 92.8
Therefore, upon mixture at 2163 K, the effect of possible contaminants must be considered. The rate coefficient for OH + H₂ = H₂O + H(3) was calculated from the principle of detailed balancing and was used to solve the set of stiff differential equations: the rate coefficient for OH + H₂ = H₂O + H was found to be unaffected by H atom addition for either case. Simultaneous optimization using NS = kOH/(NH) as the target criteria. It was found that H atom producing contaminants swept off the shock tube walls or in the test gas may be responsible. The lower temperature bound of 1550 K was set by the loss of absorption signal due to the diminishing amount of OH generated at lower temperatures.

Computer simulations were performed using the detailed reaction mechanism of Yuan et al., with the following modifications: the rate coefficients for OH + H = H₂O + H(3) was taken from the review of Oldenburg et al., the rate coefficients for O + H₂O = OH + OH(4) was taken from the review of Michael, and the reaction H + O = M + OH + M (7) was added with the rate coefficient and third body efficiencies from Masten et al. The reaction mechanism and rate coefficient expressions are given in Table 2. Reverse reaction rate coefficients were calculated from the principle of detailed balancing. NASA thermochemical data were used in all calculations. The LSODE integrator was used to solve the set of stiff differential equations describing chemical reaction under the assumed constant-density conditions for reflected shocks.

Local logarithmic response sensitivities computed for the Figure 2 experimental conditions are shown in Figure 3. Overall, NSmax and s₀ are sensitive only to reaction 1. Therefore, k₁ could be determined by matching NSmax or s₀; however, the effect of possible contaminants must be considered. This effect can be readily simulated by assuming that H atoms are present in the initial mixture. At high temperatures H atoms are generated by fast initiation reactions of the H₂O₂ system so that the addition of contaminants is found to have little effect, e.g., addition of 50 ppb H atoms to a 2% H₂O₂/98% Ar mixture at 2163 K changed s₀ from 65.4 to 65.1 μs. At low temperatures H atom contamination has a profound effect upon s₀; e.g., addition of 5 ppb H atoms to a 2% H₂O/98% O₂ mixture at 1500 K. However, the effect of possible contaminants must be considered.

**TABLE 1 (Continued)**

<table>
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<tr>
<th>T₀</th>
<th>P₀</th>
<th>Amax</th>
<th>NSmax</th>
<th>s₀</th>
<th>k₁/10¹²</th>
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<td>91966</td>
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* Units are K for T₀, atm for P₀, s⁻¹ for normalized maximum slope, μs for s₀, and cm³ mol⁻¹ s⁻¹ for k₁." k₁(NSmax).

<table>
<thead>
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<th>TABLE 2: Reaction Mechanism</th>
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<tr>
<td>reaction</td>
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<td>1. H + O₂ = OH + O</td>
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<tr>
<td>2. O + H₂ = OH + H</td>
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<tr>
<td>3. OH + H₂ = H₂O + H</td>
</tr>
<tr>
<td>4. O + H₂O = OH + OH</td>
</tr>
<tr>
<td>5. O + O = O₂</td>
</tr>
<tr>
<td>6. H + H + M = H₂ + M</td>
</tr>
<tr>
<td>7. H + O = OH + M</td>
</tr>
<tr>
<td>8. H + OH = H₂O + H</td>
</tr>
<tr>
<td>9. H + O₂ + M = HO₂ + M</td>
</tr>
<tr>
<td>10. HO₂ + H = H₂O + OH</td>
</tr>
<tr>
<td>11. HO₂ + H + O₂</td>
</tr>
<tr>
<td>12. HO₂ + H = H₂O + O</td>
</tr>
<tr>
<td>13. HO₂ + O = HO₂ + O</td>
</tr>
<tr>
<td>14. HO₂ + OH = H₂O₂ + O</td>
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<tr>
<td>15. HO₂ + HO₂ = H₂O₂ + O₂</td>
</tr>
<tr>
<td>16. H₂O₂ + M = H₂ + M</td>
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<td>17. H₂O₂ + H = H₂O + H₂</td>
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<tr>
<td>18. HO₂ + OH = H₂O₂ + O</td>
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<tr>
<td>19. HO₂ + OH = H₂O₂ + O₂</td>
</tr>
</tbody>
</table>

* Rate coefficients are in the form k = A₀ exp(-θ/T). Units are K, cm³ mol⁻¹, and s. Numbers in parentheses are powers of 10.

97.5% Ar mixture at 1234 K changed s₀ from 824 to 693 μs. This reduction in s₀ is equivalent to a 23% increase in k₁. NSmax is unaffected by H atom addition for either case.

Based upon the sensitivity and contaminant effect studies, k₁ and e(OH) were the parameters chosen for simultaneous optimization using NSmax and Amax as the target criteria. It should be noted that s₀, an integral measure of reaction progress, is affected by the details of initiation, whereas NSmax, a differential measure of growth, is determined at a point in reaction progress where memory of the initiation process is lost.
Figure 3. Sensitivity spectra for the experimental conditions in Figure 2a,b. Sensitivities are for 30% increase to Table 2 values and absorption coefficients. Reaction numbers are listed in Table 2. ■ for NS$_{max}$ sensitivity; □ for $A_{max}$ sensitivity; hashed □ for $t_{50}$ sensitivity.

Figure 4. Arrhenius plot of the experimental data for $k_1$(NS$_{max}$). The solid line is the least-squares fit to the data; $k_1$(NS$_{max}$) = 7.13 x $10^{13}$ exp($-$6957 K/T) cm$^3$ mol$^{-1}$ s$^{-1}$ (1050 K $\leq T \leq$ 2500 K). Symbols are ■ for $\phi$ = 2 mixtures, □ for $\phi$ = 5 mixtures, ○ for $\phi$ = 10 mixtures, and ● for $\phi$ = 15 mixtures (15.0% H$_2$, 0.5% O$_2$, 84.5% Ar). The data for $\phi$ = 15 mixtures were not included in the least-squares fit for $k_1$(NS$_{max}$).

The data obtained above 2500 K were not included in the analysis due to possible contamination effects (see above). However, as can be seen in Figure 4, these points lie on the extrapolated line. A least-squares fit to the data is given by:

$$k_1($NS$_{max}$) = (7.13 \pm 0.31) \times 10^{13} \exp(-6957 \pm 30\,K/T) \text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$$

with a 4% standard deviation, over the temperature range 1050–2500 K.

As was shown previously, $k_1$ and $A$(OH) can be determined using $t_{50}$ and $A_{max}$, as the optimization criteria if possible contamination effects are ignored. Results of this analysis are shown in Figure 5 where the solid line represents the least-squares fit to the data given by:

$$k_1(t_{50}) = (7.19 \pm 0.41) \times 10^{13} \exp(-7015 \pm 40\,K/T) \text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$$

with a 6% standard deviation, over the same temperature range.

The choice of optimization criteria results in two slightly different Arrhenius expressions that diverge with decreasing temperature for a maximum difference of 5% at the low-temperature extreme. If there were contamination effects, we would have expected that the expressions should have been quite different due to the dramatic effect of impurities upon $t_{50}$. The agreement of these two expressions implies that our experimental results were not significantly influenced by the presence of impurities.

A standard propagation-of-error analysis was performed for individual experimental determinations of $k_1$. Contributions to uncertainty were estimated using the measurement accuracy of the various transducers and oscilloscopes. Maximum uncertainties in the determination of $k_1$(NS$_{max}$) and $k_1(t_{50})$ were 6.0% and 7.5%, respectively. These values were then used as error limits instead of the smaller values derived from the scatter of the data about the fitted Arrhenius expressions. For typical conditions the percentage contribution to the uncertainty for individual $k_1$(NS$_{max}$) values are 54% from NS$_{max}$, 24% from $P_s$ in the temperature correction, 10% from incident shock velocity, and 10% and 2% from $\Delta X_{O_2}$ and $\Delta X_{H_2}$ of the initial mixture composition, respectively. A similar distribution of the uncertainty contributions was also obtained for $k_1(t_{50})$.

Shown in Figure 2 are computed profiles (smooth lines) obtained using the reaction mechanism in Table 2. As can be seen, the computed profiles reproduce the experiments quite well. Inspection of Figures 4 and 5 reveals that the $k_1$ values exhibit no dependence upon either composition or pressure over the ranges investigated in this study.

**Discussion**

The present determination of $k_1$ is compared to recent experimental and modeling studies in Table 3 and Figure 6. There is good agreement with the expressions of Shin and Michael and Yang et al.

The study of Pirraglia et al. (PMSK), flash photolysis followed by pseudo-first-order decay of H atoms, has taken on great importance because it contains the only data for $k_1$ below 1050 K. As a result, it has been used in most of the more recent studies either for comparison or combined with other data to make Arrhenius or non-Arrhenius expressions. While the expressions determined by PMSK and in this study agree within 20% over the mutual temperature range, their
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**TABLE 3: Comparison of Rate Coefficient Expressions**

<table>
<thead>
<tr>
<th>Authors</th>
<th>T range</th>
<th>A</th>
<th>n</th>
<th>θ</th>
<th>ref</th>
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<td>PMSK</td>
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<td>8119 ± 139</td>
<td>23</td>
<td>c</td>
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<td>MHB</td>
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<td>-0.927</td>
<td>8493</td>
<td>14</td>
<td>e</td>
</tr>
<tr>
<td>SM</td>
<td>1103–2055</td>
<td>(6.93 ± 0.96) × 10¹³</td>
<td>0.00</td>
<td>6917 ± 193</td>
<td>21</td>
<td>d</td>
</tr>
<tr>
<td>DH</td>
<td>960–5300</td>
<td>(9.76 ± 0.72) × 10¹³</td>
<td>0.00</td>
<td>7474 ± 122</td>
<td>24</td>
<td>f</td>
</tr>
<tr>
<td>YFMHB</td>
<td>1336–3370</td>
<td>8.30 ± 10¹¹</td>
<td>0.00</td>
<td>7253</td>
<td>27</td>
<td>g</td>
</tr>
<tr>
<td>YGSF</td>
<td>1100–3550</td>
<td>(7.60 ± 0.70) × 10¹³</td>
<td>0.00</td>
<td>7065 ± 140</td>
<td>22</td>
<td>h</td>
</tr>
<tr>
<td>RHR</td>
<td>1050–2500</td>
<td>(7.13 ± 0.31) × 10¹³</td>
<td>0.00</td>
<td>6957 ± 30</td>
<td>this study</td>
<td>i</td>
</tr>
</tbody>
</table>

*Rate coefficients are in the form k = A exp(–θ/T). Units are K, cm³, mol, and s. *Abbreviations explained in text. 16% mean deviation.

1σ deviation. *σ error = 0.05. *Uncertainties in 95% confidence level; combined results with SM, MHB, PMSK data. 9% 1σ deviation; optimization using YWYFR and MHB data. 6% deviation, k(T NS).*

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**Figure 6.** Comparison of the present results for k₁ to the previous experimental studies.

Temperature dependences are very different. At 1050 K our expression is 22% higher, and at 1700 K our expression is 19% lower. A recent review[16] notes that there may have been bias in the data set at low temperatures (T < 1200 K) due to a systematic overestimation of HO₂ production. This may account for the high-temperature dependence observed by PMSK.

Masten et al.[17] (MHB) performed a dual beam laser absorption study of OH radical similar to ours. They obtained an expression that is 7.5% higher at 2500 K and 7.0% lower at 1450 K than the present study; however, our expression is contained within the MHB error limits (±10%). For the incident shock condition shown in Figure 3 of MHB our value of k₁ is 2% lower than their value, and as might be expected, our predicted profile is in excellent agreement with the MHB experimental profile. For the reflected shock condition shown in their Figure 5 our value of k₁ is 10% lower. Nonetheless, our predicted profile is again in good agreement with their experimental profile. Substitution of our k₁ expression into the MHB mechanism required a factor of 2.5 increase in the value of the initiation reaction, k₁₁ (H₂ + H = H₂ + O₂), to match the profile. This is an increase of only 40% above the value of k₁₁ used in the present study. In their analysis MHB treated k₁ as a profile shifting parameter, the shape of the profile being controlled by k₁₁.

Yuan et al.[18] (YWYFR) performed a single-beam laser absorption study of OH radical. Five active parameters, k₁, k₂, k₃, k₁₁, and ΔH₂98(HO₂), were simultaneously optimized using the solution mapping method.[25] Compared to the present results in the common temperature range, 1150–2500 K, the k₁ values of YWYFR are on average 14% lower, but the error limits are overlapped. These authors also reported that when using MHB’s secondary reaction rate coefficients, k₂, k₃, and k₁₁, a slightly different expression resulted, 1.71 × 10¹⁷T⁻⁰.⁹³² exp(–8498 K/T), which differs from their previous expression by 3% and shows the effect of the choice of secondary reaction rate coefficients upon the determination of k₁.

Shin and Michael[21] (SM) performed a laser photolysis study of H atom depletion under pseudo-first-order conditions. As shown in Figure 6, the k₁ values of SM and those of the present study are in agreement over the temperature range 1100–2055 K. Their k₁ values, derived from the measured slope of ln(absorbance), are independent of impurity effects. SM corrected for boundary layer effects as was done in the present study.[10,26]

Du and Hessler[22] (DH) performed a flash absorption study of OH radical profiles in shock-heated H₂/O₂/Kr test gas. They combined their results with the data of MHB, PMSK, and SM and obtained an expression that is 16% lower at 1050 K and 11% higher at 2500 K than the present results. In their evaluation DH introduced a profile shift parameter, x₁, that was needed to shift their calculated profiles to longer distances in order to match the experimental profiles. They associated x₁ with the incubation time of H₂ dissociation, the main initiation channel at high temperature. However, we are able to model their Figure 3 experimental profile using the Table 2 mechanism without any profile shifting. This comparison is shown in Figure 7, where the solid line is our predicted absorption profile and the dotted lines are the upper and lower noise band of the DH profile. For this condition DH used a 0.783 mm shift of their calculated profile. Our prediction is well within the noise band, although approaching the high end at long distances, where the profile is controlled by H₂ decomposition. Indeed, at all times, the profile is more sensitive to the rate coefficient of H + H + M = H₂ + M (6) than to all other reactions, including reaction 1. This can be seen in Figure 7 where the upper filled boxes and the lower open boxes represent the extent of profile shift for ±20% variations in k₁ and k₆, respectively.

Recently, the data of YWYFR and MHB were subjected to a simultaneous optimization using two different model responses by Yu et al.[27] (YFMHB): the characteristic times, t₁, and the time difference, Δt, defined as Δt = t₂₅ – t₁. The MHB data yielded nearly identical k₁ expressions for both model responses while those of YWYFR were noticeably different, with k₁(t₁) having a nonzero temperature dependence of the preexponential factor and being 15% lower than k₁(Δt) at 2150 K. There was reasonable agreement between the YWYFR k₁(Δt) and both the MHB k₁ expressions (which were nearly identical). An explanation for the difference between the YWYFR k₁(t₁) and k₁(Δt) was proposed on the basis of the effect of vibrational nonequilibrium of O₂. The high-temperature YWYFR data were taken at short reaction times where this effect would be most pronounced. This is akin to the explanation given by DH for
Figure 7. Comparison of our computed profile to the experimental profile of Du and Hessler's Figure 3 condition. The solid line is the absorption profile computed using the Table 2 reaction mechanism with $x_c = 0$. The dotted lines are upper and lower noise band derived from the DH profile. The early part of the experimental signal is dominated by shock passage transients. Filled and open boxes represent the extent of profile changes for ±20% variation of $k_1 (H + O_2 = OH + O)$ and $k_2 (H + H + M = H_2 + M)$, respectively.

The possible effect of O$_2$ vibrational relaxation on hydrogen combustion has important implications for the prediction of air-breathing hypersonic propulsion system performance. Such systems would be hydrogen fueled and have characteristic chemical reaction times much shorter than 100 μs. In order to quantify the effect of O$_2$ vibrational relaxation, a series of experiments were run using the YWYFR Series E composition in the pressure and temperature range where the effect should be most apparent, i.e., 2.4—3.0 atm and 1905—2380 K. Unlike the case of the YWYFR data, we did not see a difference between the $k_1$ value determined using either $t_{50}$ or $\Delta t$ as the modeling criterion. The experimental values of $t_{50}$ and $\Delta t$ are shorter than predicted using the Table 2 mechanism, on average by 2% (0.6 μs) and 5% (0.3 μs), respectively. While arbitrary time accuracy may be achieved in simulations, differences of this scale, although they are discernible, are not particularly meaningful. Nonetheless, the Table 2 mechanism does account for the $t_{50}$, $\Delta t$, and NS$_{max}$ values for each experiment. At these conditions there is exquisite sensitivity to $t_{50}$ as modeling criterion—a 0.1 μs change requires a 1% change in $k_1$, while sensitivity to $\Delta t$ was smaller. The optimized $k_1$ values for these experiments differ on average by 4% (within our uncertainty limits) from our recommended expression. Individual experiments required adjustments between −3% and +8%. We are not required to invoke O$_2$ vibrational relaxation to explain our short reaction time data as both $t_{50}$ and $\Delta t$ are predicted equally well using our mechanism without additional constraints. Belles and Lauver have previously shown that O$_2$ vibrational relaxation is not required to explain the induction delay lengthening at short times in H$_2$/O$_2$ mixtures as had been proposed by Schott and Kinsey.

Yang et al. (YGFS) performed a single-beam laser absorption study of OH radical. It was a reinvestigation that supplemented previous work on the title reaction. An iterative optimization using eight time-difference responses (e.g., $t_{50} - t_{40}$) yielded a rate coefficient expression that is 5% lower at 1850 K and 5% higher at 2500 K than our expression. YGFS then combined their data with that of SM and obtained a new expression that is also within our error bounds, being 4% lower at 1100 K and 2% higher at 2500 K.

Both experimental and theoretical proposals have been made for the temperature dependence of the preexponential factor of $k_1$. Nonzero experimental values are reported by Schott (−0.907), YWYFR (−0.927), and MHB (−0.7, obtained from the combination of MHB and PMSK data). Miller's theoretical calculation gave −0.816$^{23,33}$ obtained using quasiclassical trajectory and quantum mechanical threshold methods on the potential energy surface of Melius and Blint. He attributed the negative temperature dependence to the nonstatistical "recrossing" effects especially at high temperatures. PMSK, MHB (MHB data only), SM, DH, YFMHB, YGFS, and the present study do not find a temperature dependence for the preexponential factor. Recently, Varandas et al. (VBP) calculated the thermal rate coefficient using various versions of quasiclassical trajectory method at 1000, 1750, 2000, 2500, and 3000 K. In the calculation, the fourth version of their double many-body expansion potential energy surface for the ground state of HO$_2$ was utilized, which reproduces the most accurate estimates of the experimental dissociation energy, equilibrium geometry, and quadratic force constants. Their calculations showed no temperature dependence for the preexponential factor.

There exists reasonable agreement between the results of this study and most of the recent evaluations of $k_1$; and so it is possible to achieve a consensus expression, shown in Figure 8, given by

$$k_1 = 7.82 \times 10^{13} \exp(-7105 K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 960—5300 K, with an uncertainty of 6%. We developed this expression in the following fashion. The expressions of PMSK, SM, DH, YFMHB, YGFS, and the present study were converted to a series of "data points" evenly spaced in 1/T over their temperature ranges. A weighted least-squares fit was then obtained with the weighting factor taken as the inverse of the uncertainty limits for the Arrhenius expressions reported in the individual studies. The data of PMSK and SM were used to develop the DH expression, and the data of SM were used to develop the YGFS expression.
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Accordingly, their weighting factors were reduced, PMSK by half and SM by two-thirds, to correct for their overrepresentation. An Arrhenius expression was assumed as there is neither an experimental nor, currently, a theoretical basis for curvature.

Conclusions

The rate coefficient of the reaction H + O₂ = OH + O (1) was determined using OH laser absorption spectroscopy behind reflected shock waves over the temperature range 1050–2500 K and the pressure range 0.7–4.0 atm. Eight different mixtures and three different stoichiometries were used. Two distinct and independent criteria were employed in the evaluation of $k_1$, namely, normalized maximum slope and the characteristic time, $t_{50}$. Our recommended expression for $k_1$, obtained using normalized maximum slope, is

$$k_1 = 7.13 \times 10^{13} \exp(-6957 K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

with an uncertainty of 6%. This expression agrees with that of SM and with the computational results of VBP. We neither support a curved rate coefficient expression nor find evidence of composition dependence upon the determination of $k_1$. Without confirmation of the PMSK results below 1050 K, there is neither an experimental nor, currently, a theoretical basis for curvature. Critical review of recent $k_1$ determinations yields the consensus expression

$$k_1 = 7.82 \times 10^{13} \exp(-7105 K/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

over the temperature range 960–5300 K.

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References and Notes

(3) Lewis, R. S.; Watson, R. T. J. Phys. Chem. 1980, 84, 3495.

(37) "... their faces were not all the same, yet not unalike, but rather the way sisters ought to be"—Ovid, Metamorphoses 2.13-14.