Shock Tube and Modeling Study of the H + O₂ = OH + O Reaction over a Wide Range of Composition, Pressure, and Temperature

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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 mixtures and three stoichiometries were used. Two distinct and independent criteria were employed in the evaluation of k₁. Our recommended expression for k₁ is

\[
k₁ = 7.13 \times 10^{13} \exp(-6957 \text{K/T}) \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}
\]

with a statistical uncertainty of 6%. A critical review of recent evaluations of k₁ yields a consensus expression given by

\[
k₁ = 7.82 \times 10^{13} \exp(-7105 \text{K/T}) \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}
\]

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 k₁.

Introduction

The reaction between hydrogen atom and oxygen molecule,

\[
H + O₂ → OH + O \quad (ΔH_{298}^0 = 70.2 \text{kJ mol}^{-1}) \quad (1)
\]
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.¹ That this reaction is rate controlling invariably found to be sensitive to the rate coefficient of this reaction. Thus, ignition delays and flame speeds, important and easily measurable combustion characteristics, are invariably 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.² (BDHL) reviewed the available data and recommended the rate coefficient expression

\[
k₁ = 2.2 \times 10^{14} \exp(-8450 \text{K/T}) \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}
\]

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).³,⁴ In 1973, Schott⁵ measured the exponential growth rate of CO₂ chemiluminescence in shock-heated H₂/CO/O/Ar mixtures and reported a rate coefficient expression with a temperature-dependent preexponential factor,

\[
k₁ = 1.22 \times 10^{7} T^{-0.907} \exp(-8369 \text{K/T}) \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}
\]

For over a decade these two expressions formed the upper, BDHL, and lower, Schott, accepted limits for k₁. In 1984, Warnatz⁶ reviewed the available data and recommended Schott’s expression. In 1985, Frank and Just⁷ measured O and H atom concentration profiles in shock-heated H₂/O₂/N₂/O/Ar mixtures and reported the rate coefficient expression

\[
k₁ = 2.44 \times 10^{14} \exp(-8697 \text{K/T}) \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}
\]

which agreed well with the recommended value of BDHL: no temperature dependence of the preexponential factor was found. The position of experiment and review had been reversed with


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Study of the $H + O_2 = OH + O$ Reaction

![Schematic diagram of the experimental apparatus.](image)

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 F$_2$(S) line of the (0,0) band of the $A^2S^+ \rightarrow X^2Π$ transition at 310.032 nm (air). A Coherent CR-699-21 ring-dye laser running Kiton Red 620 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-dyneode configuration to ensure optimum linearity. High-speed buffer/amplifiers were used to isolate the anodes. An overall electronic time constant of 0.2 µs 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 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 CI-I4 <0.3 ppm); O$_2$, 99.6% (Linde Zero Grade, THC as CH$_4$ <0.3 ppm); Ar, 99.96% (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 superequilibrium 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, $A_{max} = (1 - \frac{d(Ib)/dt}{dmax})$, $NS_{max} = -\frac{d(\text{Ib})/dt}{A_{max}}$, and one characteristic time, $t_{50}$, the time at which the absorbed light intensity has reached 50% of $A_{max}$. These three observables were chosen based upon sensitivity analysis using a trial H$_2$/O$_2$ reaction mechanism. It has been shown previously$^{12,13}$ 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>$\Delta _s$</th>
<th>$N _s$</th>
<th>$\beta _s$</th>
<th>$k _s \times 10^4$</th>
<th>$T _s$</th>
<th>$P _s$</th>
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<th>$N _s$</th>
<th>$\beta _s$</th>
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<td>0.96</td>
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<td>2.93</td>
<td>0.104</td>
<td>1115</td>
<td>2.248</td>
<td>0.492</td>
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<td>1115</td>
<td>2.248</td>
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<td>18.471</td>
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<tr>
<td>2.289</td>
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<td>836</td>
<td>0.124</td>
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</table>

### Conditions and Results

- **4.0% H₂, 1.0% O₂, 95.0% Ar ($\phi = 2$)**
- **2.0% H₂, 0.5% O₂, 97.5% Ar ($\phi = 2$)**
- **0.4% H₂, 0.1% O₂, 99.5% Ar ($\phi = 2$)**
- **5.0% H₂, 0.5% O₂, 94.5% Ar ($\phi = 5$)**

Ryu et al.
This effect can be readily simulated by assuming that H atoms are present in the initial mixture. At high temperatures H atoms are sensitive to reaction 1. Therefore, $k_1$ could be determined by matching $\alpha_{\text{max}}$ or $\theta$, 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 H2/O2 system so that the addition of contaminants is found to have little effect, e.g., addition of 50 ppb H atoms to a 2% H2/O2 mixture 97.8% Ar mixture at 2163 K changed $\theta$ from 824 to 693.$^b$ This reduction in $\theta$ is equivalent to a 23% increase in $k_1$. $\alpha_{\text{max}}$ is unaffected by H atom addition for either case.

Based upon the sensitivity and contaminant effect studies, $k_1$ and $\epsilon$(OH) were the parameters chosen for simultaneous optimization using $\alpha_{\text{max}}$ and $\alpha_{\text{max}}$ as the target criteria. It should be noted that $\theta$, an integral measure of reaction progress, is affected by the details of initiation, whereas $\alpha_{\text{max}}$, a differential measure of growth, is determined at a point in reaction progress where memory of the initiation process is lost.

### Table 1 (Continued)

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<tr>
<th>$T_s$</th>
<th>$P_s$</th>
<th>$\alpha_{\text{max}}$</th>
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<th>$k_1$</th>
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<td>0.150</td>
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### Table 2: Reaction Mechanism

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<th>n</th>
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<tr>
<td>1. $H + O_2 = OH + O$</td>
<td>7.13 (+13)</td>
<td>0.0</td>
<td>6957 this study</td>
</tr>
<tr>
<td>2. $O + H_2 = OH + H$</td>
<td>1.87 (+14)</td>
<td>0.0</td>
<td>6854 38</td>
</tr>
<tr>
<td>3. $OH + H_2 = H_2O + H$</td>
<td>2.14 (+08)</td>
<td>1.52</td>
<td>1736 15</td>
</tr>
<tr>
<td>4. $O + H_2O = OH + OH$</td>
<td>4.51 (+04)</td>
<td>2.70</td>
<td>7323 16</td>
</tr>
<tr>
<td>5. $O + O = O_2$</td>
<td>1.00 (+17)</td>
<td>-1.0</td>
<td>0 12</td>
</tr>
<tr>
<td>6. $H + H = H_2$</td>
<td>6.40 (+17)</td>
<td>-1.0</td>
<td>0 12</td>
</tr>
<tr>
<td>7. $O + O = O_2$</td>
<td>6.17 (+16)</td>
<td>-0.6</td>
<td>0 17</td>
</tr>
<tr>
<td>8. $H + O = HO + O$</td>
<td>8.40 (+21)</td>
<td>-2.0</td>
<td>0 12</td>
</tr>
<tr>
<td>9. $H + O = HO + O$</td>
<td>7.00 (+17)</td>
<td>-0.8</td>
<td>0 12</td>
</tr>
<tr>
<td>10. $H + O = H_2 + O$</td>
<td>6.17 (+16)</td>
<td>-0.6</td>
<td>0 17</td>
</tr>
<tr>
<td>11. $H_2O = HO + OH$</td>
<td>2.41 (+16)</td>
<td>-0.2</td>
<td>0 12</td>
</tr>
<tr>
<td>12. $H_2O + H = H_2 + OH$</td>
<td>2.00 (+13)</td>
<td>0.0</td>
<td>0 1</td>
</tr>
<tr>
<td>13. $H_2O + H = H_2O_2$</td>
<td>1.06 (+11)</td>
<td>-0.5</td>
<td>0 45</td>
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<tr>
<td>14. $H_2O + H = H_2 + O$</td>
<td>1.00 (+17)</td>
<td>-0.8</td>
<td>0 12</td>
</tr>
</tbody>
</table>

$^a$ Units are K for $T_s$, atm for $P_s$, s$^{-1}$ for normalized maximum slope, $\mu$s for $\theta_{\text{max}}$, and cm$^3$ mol$^{-1}$ s$^{-1}$ for $k_1$. $^b$ $k_1$ ($\alpha_{\text{max}}$).
2. Sensitivity

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,

sensitivity; □, for A, sensitivity; ○, for t, sensitivity; hashed ○, for t, sensitivity.

3. Sensitivity

Figure 4. Arrhenius plot of the experimental data for k,(NS). The solid line is the least-squares fit to the data; k,(NS) = 7.13 x 10^13 exp(-6957 K/T) cm^3 mol^-1 s^-1 (1050 K ≤ T ≤ 2500 K). Symbols are □ for φ = 2 mixtures, ○ for φ = 5 mixtures, ○ for φ = 10 mixtures, and ● for φ = 15 mixtures (15.0% H_2, 0.5% O_2, 84.5% Ar). The data for φ = 15 mixtures were not included in the least-squares fit for k,(NS).

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

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

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

As was shown previously, k_1 and ε(OH) can be determined using t_50 and A_50, 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

\[ k_1(t_50) = (7.19 \pm 0.41) \times 10^{13} \exp(-7015 \pm 40 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \]

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(\text{NS}) 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(\text{NS}) values are 54% from NS, 24% from P_5 in the temperature correction, 10% from incident shock velocity, and 10% and 2% from ΔX_O_2 and ΔX_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 to make Arrhenius or non-Arrhenius expressions. While the expressions determined by PMK and in this study agree within 20% over the mutual temperature range, their...
Table 3: Comparison of Rate Coefficient Expressions

<table>
<thead>
<tr>
<th>Authors</th>
<th>T Range</th>
<th>A</th>
<th>n</th>
<th>$\theta$</th>
<th>Ref</th>
<th>Notes</th>
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<tr>
<td>PMSK</td>
<td>962-1750</td>
<td>$(1.68 \pm 0.19) \times 10^{14}$</td>
<td>0.00</td>
<td>8119 ± 139</td>
<td>23</td>
<td>c</td>
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<td>MHB</td>
<td>1450-3370</td>
<td>$(9.33 \pm 0.40) \times 10^{13}$</td>
<td>0.00</td>
<td>7448 ± 86</td>
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<td>24</td>
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<td>RHR</td>
<td>1050-2500</td>
<td>$(7.13 \pm 0.31) \times 10^{13}$</td>
<td>0.00</td>
<td>6957 ± 30</td>
<td>this study i</td>
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</tbody>
</table>

*Rate coefficients are in the form $k = A^\theta \exp(-\Delta/kT)$. Units are K, cm$^{-3}$ mol$^{-1}$ s$^{-1}$. Abbreviations explained in text. *16% mean deviation.

Figure 6. Comparison of the present results for $k_1$ to the previous experimental studies.

The 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 notes that there may have been bias in the data set at low temperatures ($T < 1200$ K) due to a systematic overestimation of HO$_2$ production. This may account for the high-temperature dependence observed by PMSK.

Masten et al. (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 ($\pm10\%$). For the incident shock condition shown in Figure 3 of MHB our value of $k_1$ 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 $k_1$ is 10% lower. Nonetheless, our predicted profile is again in good agreement with their experimental profile. Substitution of our $k_1$ expression into the MHB mechanism required a factor of 2.5 increase in the value of the initiation reaction, $k_1$ of $H_2 + H_2 + O_2$, to match the profile. This is an increase of only 40% above the value of $k_1$ used in the present study. In their analysis MHB treated $k_1$ as a profile shifting parameter, the shape of the profile being controlled by $k_1$.

Yuan et al. (YWYFR) performed a single-beam laser absorption study of OH radical. Five active parameters, $k_1$, $k_2$, $k_3$, $k_1$, and $\Delta H^\circ_{298}(H_2O_2)$, were simultaneously optimized using the solution mapping method. Compared to the present results in the common temperature range, 1150–2500 K, the $k_1$ 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, $k_2$, $k_3$, and $k_11$, a slightly different expression resulted, $1.71 \times 10^{17}T^{-0.932} \exp(-8498K/T)$, which differs from their previous expression by 3% and shows the effect of the choice of secondary reaction rate coefficients upon the determination of $k_1$.

Shin and Michael (SM) performed a laser photolysis study of H atom depletion under pseudo-first-order conditions. As shown in Figure 6, the $k_1$ values of SM and those of the present study are in agreement over the temperature range 1100–2055 K. Their $k_1$ values, derived from the measured slope of Im- (absorbance)$_b$, are independent of impurity effects. SM corrected for boundary layer effects as was done in the present study.

Du and Hessler (DH) performed a flash absorption study of OH radical profiles in shock-heated H$_2$O/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, $x_c$, that was needed to shift their calculated profiles to longer distances in order to match the experimental profiles. They associated $x_c$ with the incubation time of H$_2$ 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 approximating the high end at long distances, where the profile is controlled by $H_2$ decomposition. Indeed, at all times, the profile is more sensitive to the rate coefficient of $H + H + M = H_2 + M$ (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 $\pm20\%$ variations in $k_1$ and $k_6$, respectively.

Recently, the data of YWYFR and MHB were subjected to a simultaneous optimization using two different model responses by Yu et al. (YFMBH): the characteristic times, $t_i$, and the time difference, $\Delta t$, defined as $\Delta t = t_3 - t_2$. The MHB data yielded nearly identical $k_1$ expressions for both model responses while those of YWYFR were noticeably different, with $k_1(t_3)$ having a nonzero temperature dependence of the preexponential factor and being 15% lower than $k_1(t_3)$ at 2150 K. There was reasonable agreement between the YWYFR $k_1(\Delta t)$ and both the MHB $k_1$ expressions (which were nearly identical).

An explanation for the difference between the YWYFR $k_1(t_3)$ and $k_1(\Delta t)$ was proposed on the basis of the effect of vibrational nonequilibrium of O$_2$. 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 Hesseler's Figure 3 condition. The solid line is the absorption profile computed using the Table 2 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 $k_0 (H + H + M = H_2 + M)$, respectively.

The profile shift parameter included in their study. YFMHB suggest an Arrhenius expression based upon the $\Delta r$ response surface that is within our error bounds, being 3% higher at 2500 K and 7% lower at 1336 K than the present study.

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 $\mu$s. 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 $t_{so}$ or $\Delta t$ as the modeling criterion. The experimental values of $t_{so}$ and $\Delta t$ are shorter than predicted using the Table 2 mechanism, on average by 2% (0.6 $\mu$s) and 5% (0.3 $\mu$s), 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 $t_{so}$, $\Delta t$, and $N_{so}$ values for each experiment. At these conditions there is exquisite sensitivity to $t_{so}$ as modeling criterion—a 0.1 $\mu$s 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 $t_{so}$ and $\Delta t$ are predicted equally well using our mechanism without additional constraints. Belles and Lauer 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. (YGSF) performed a single-beam laser absorption study of OH radical. It was a reinvestigation that supplanted previous work on the title reaction. An iterative optimization using eight time-difference responses (e.g., $t_{so} - t_{40}$) yielded a rate coefficient expression that is 5% lower at 1850 K and 5% higher at 2500 K than our expression. YGSF 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 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, YGSF, 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 obtained with the state of $H_2O$ 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, simply 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, YGSF, 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 YGSF 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

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

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

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

over the temperature range 960–5300 K.

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References and Notes

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