A Shock Tube Study of the CO + OH Reaction Near the Low-Pressure Limit

Ehson Fawad Nasir, and Aamir Farooq

J. Phys. Chem. A, Just Accepted Manuscript • DOI: 10.1021/acs.jpca.6b01322 • Publication Date (Web): 16 May 2016

Downloaded from http://pubs.acs.org on May 22, 2016

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
A Shock Tube Study of the CO + OH Reaction Near the Low-Pressure Limit

Ehson F. Nasir$^1$, Aamir Farooq*$^1$

$^1$ King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center (CCRC), Physical Science and Engineering Division (PSE), Thuwal 23955-6900, Saudi Arabia

*Corresponding Author:

Email: aamir.farooq@kaust.edu.sa

Phone: +966-128082704
Abstract

Rate coefficients for the reaction between carbon monoxide and hydroxyl radical were measured behind reflected shock waves over 700 – 1230 K and 1.2 – 9.8 bar. The temperature/pressure conditions correspond to the predicted low-pressure limit of this reaction, where the channel leading to carbon dioxide formation is dominant. The reaction rate coefficients were inferred by measuring the formation of carbon dioxide using quantum cascade laser absorption near 4.2 µm. Experiments were performed under pseudo-first order conditions with tert-butyl hydroperoxide (TBHP) as the OH precursor. Using ultraviolet laser absorption by OH radicals, the TBHP decomposition rate was measured to quantify potential facility effects under extremely dilute conditions used here. The measured CO + OH rate coefficients are provided in Arrhenius form for three different pressure ranges:

\[ k_{\text{CO+OH}}(1.2 - 1.6 \text{ bar}) = (9.14 \pm 2.17) \times 10^{-13} \exp\left(-\frac{1265 \pm 190}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k_{\text{CO+OH}}(4.3 - 5.1 \text{ bar}) = (8.70 \pm 0.84) \times 10^{-13} \exp\left(-\frac{1156 \pm 83}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k_{\text{CO+OH}}(9.6 - 9.8 \text{ bar}) = (7.48 \pm 1.92) \times 10^{-13} \exp\left(-\frac{929 \pm 192}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

The measured rate coefficients are found to be lower than the master equation modeling results by Weston et al. [J. Phys. Chem. A, 117 (2013) 821] at 819 K and in closer agreement with the expression provided by Joshi and Wang [Int. J. Chem. Kinet., 38 (2006) 57].
1. Introduction

The reaction between carbon monoxide and the hydroxyl radical is considered the principal pathway for heat release and carbon dioxide formation in most hydrocarbon combustion systems.

\[ \text{CO} + \text{OH} \rightarrow \text{Products} \]  

Previous studies have shown that the laminar flame speed has the second highest sensitivity to the CO + OH reaction (after the H + O\(_2\) chain-branching reaction), particularly for large alkanes\(^1\) and oxygenates\(^3\). As a result of its significance, the reaction has been the focus of many experimental and modeling efforts. The relevant references for these works can be found in recent publications by Joshi and Wang\(^4\) and by Weston et al.\(^5\) The CO + OH reaction has two product pathways:

\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \]  

\[ \text{CO} + \text{OH} \rightarrow \text{HOCO} \]  

The branching ratio between these pathways is heavily in favor of \(k_{1a}\) in the low-pressure limit of the reaction, whereas at high pressure, the \(k_{1b}\) channel gains significance due to the stabilization of the activated complex HOCO. For most combustion applications, the rate remains within the low-pressure limit as given, for example, by the expression in Joshi and Wang\(^4\).

Measurements of this rate have been carried out in various experimental arrangements. Brabbs et al.\(^6\) performed an indirect rate determination for the temperature range 1300-1900 K using a shock tube with H\(_2\)-O\(_2\)-CO mixtures. Similar mixtures were used by Vandooren et al.\(^7\) in a lean flame where the rate was determined using a molecular beam mass spectrometer. These rate determinations were indirect in nature as the experimental conditions were not uniquely...
sensitive to the target rate and, therefore, required additional assumptions to deduce the rate constant with the help of a kinetic model. More direct determinations of this rate at high temperature were performed by Wooldridge and Hanson\textsuperscript{8} using HNO\textsubscript{3} as the OH precursor. Lower temperature (<1100 K) studies were carried out in flow reactor experiments using excitation techniques such as flash photolysis\textsuperscript{9-11} or electron beam excitation\textsuperscript{12} to generate OH from the appropriate gas mixtures. It should be noted that, with the exception of Fulle et al.\textsuperscript{10}, all previous low-temperature determinations were well within the low-pressure limit of \( k_1 \). In low-temperature combustion environments, such as HCCI engines, the operating conditions are typically not very far from the low-pressure limit and, therefore, it is important to study the CO + OH reaction in the vicinity of the low-pressure limit.

In this work, rate coefficients for \( k_{1a} \) were measured near the low-pressure limit in pseudo-first order shock tube experiments. Hydroxyl radicals were generated by thermal decomposition of tert-butyl hydroperoxide (TBHP) which is known to be a clean OH precursor\textsuperscript{13}. A sensitive infrared laser absorption sensor was used to measure CO\textsubscript{2} concentration profiles which were found to be mainly sensitive to \( k_{1a} \) and the TBHP decomposition rate, also measured as part of this study. The use of highly sensitive laser absorption technique allowed for a more accurate determination of the rate coefficient compared to previous low-temperature studies. This work represents, to our knowledge, the first measurement of \( k_{1a} \) at low temperatures in a shock tube facility.
2. Experimental Method

2.1 Shock Tube Facility

All experiments were carried out behind reflected shock waves in the low-pressure shock tube facility at King Abdullah University of Science and Technology (KAUST). The facility has been described previously and only a brief overview will be provided here. The shock tube is electro-polished with an inner diameter of 14.2 cm and a driven section length of 9 m. The length of the driver section can be increased up to 9 m depending on the required test times. The test times in this work were 1-2 milliseconds and the uncertainties in reflected shock conditions (T, P) were less than 1%. The laser diagnostics (CO\textsubscript{2} and OH) used in this study were aligned at an axial plane 2 cm from the shock tube endwall, as shown in Fig. 1. High-purity (99.999%) argon and carbon monoxide were used for preparing reactant mixtures. A 70% TBHP solution in water was supplied by Sigma-Aldrich. Gaseous mixtures were prepared manometrically in a 24-litre magnetically-stirred mixing vessel. The shock tube was turbo-pumped between experiments down to 5 x 10\textsuperscript{-5} mbar to maintain high purity of the reactive environment.

![Experimental schematic showing the planar cross-section of the shock tube 2 cm from the endwall.](image)

**2.2 Hydroxyl Precursor and Laser Diagnostic**

Several previous investigations of rate measurements for reactions involving OH have employed TBHP as a fast, clean source of OH over a wide temperature range (800 – 1300 K).\textsuperscript{15-17} Hydroxyl radicals are generated via the following decomposition reaction:

$$\text{TBHP} \rightarrow \text{t-Butoxy} + \text{OH}$$  \hspace{1cm} (2)

For temperatures greater than 1000 K, TBHP decomposition is near instantaneous after the arrival of the reflected shock wave. This allows the initial TBHP concentration to be determined from the peak OH yield via an \textit{in-situ} OH diagnostic. This determination is necessary due to the adsorption of TBHP to the mixing vessel and shock tube walls which results in a lower TBHP concentration than that determined manometrically. For temperatures lower than 1000 K, the time scale of TBHP decomposition is longer and therefore the peak OH yield no longer provides a measure of the initial TBHP concentration. In this study, high- and low- temperature measurements were alternated so that the initial TBHP concentration determined from the high-temperature cases can be used in the low-temperature cases. The TBHP concentration measured using this method did not vary by more than 10% between consecutive high-temperature cases.

Based on the measured TBHP concentration, the water vapor mole fraction was estimated through Rault’s law. Previously, Pang et al.\textsuperscript{13} had shown that water vapor does not have any significant effect on TBHP kinetics under highly dilute conditions.

A ring-dye laser system with external frequency doubling, details of which can be found in the work by Badra et al.\textsuperscript{18}, was used to generate laser light near 306 nm to measure OH mole fraction using the Beer-Lambert relation, $I/I_0 = \exp(-k_{\text{OH}}X_{\text{OH}}PL)$. Here, $I_0$ and $I$ refer to incident and transmitted laser intensities respectively, $k_{\text{OH}}$ is the absorption coefficient, $X_{\text{OH}}$ is the OH mole fraction, $P$ is the pressure and $L$ is the absorption path length (inner diameter of shock tube).
tube). For the conditions of interest, this diagnostic provides a noise-limiting detection limit of 0.1 ppm.

### 2.2 CO₂ Laser Diagnostic

An external cavity quantum cascade laser (Daylight Solutions) operating near 4.2 µm was used to measure CO₂ concentration via the R(32) ro-vibrational transition in the ν₃ band of CO₂. Absorption cross-sections at the peak of this line were measured in separate experiments of shock-heated CO₂-Ar mixtures over 700 – 2000 K and 1 – 10 bar. These measurements are provided in the Supplementary Material. As with the OH diagnostic, the CO₂ concentrations were calculated using the Beer-Lambert law. Compared with previous diagnostics based on the ν₃ band¹⁹, this sensor provides much higher sensitivity for these conditions with a noise-limiting detection limit of 2 ppm. Since CO₂ in the ambient air also strongly absorbs the laser intensity at this wavelength, a nitrogen purging setup was used over the entire laser path from the laser source to the photo-detector, as shown in Fig. 1.

### 3. Results and Discussion

#### 3.1 Sensitivity Analyses

The experimental results were modeled using the modified JetSurF 1.0 mechanism, which contains TBHP reactions provided by Pang et al.¹³. Sensitivity analyses and kinetic simulations were performed using the ChemKin-Pro software package. Figures 2 and 3 show the reactions contributing significantly to the sensitivity coefficient of OH and CO₂, respectively. From these analyses, it is evident that the CO₂ concentration profile is more sensitive to the target rate $k_{1a}$ as compared to the OH profile for which other reactions are more significant.
contributors. Therefore, in this work, $k_{1a}$ was determined by fitting the kinetic simulation results to the measured CO$_2$ profiles.

![Graph](image)

**Fig. 2.** Hydroxyl sensitivity analysis using the modified JetSurF mechanism$^{20}$. Simulation conditions: $T = 862$ K, $P = 1.52$ bar, 120 ppm TBHP / 180 ppm H$_2$O / 0.5% CO / Ar (bath gas).

![Graph](image)

**Fig. 3.** Carbon dioxide sensitivity analysis using the mechanism and conditions of Fig. 2.
3.2 TBHP Kinetics

Figure 2 illustrated the significant contribution of $k_2$ (TBHP decomposition) on the CO$_2$ sensitivity, indicating that the uncertainty in this rate will affect determination of $k_{1a}$. Direct measurements of $k_2$ using TBHP/Ar mixtures have only been performed previously by Pang et al.$^{13}$ We decided to make a similar rate determination for $k_2$ to compare against results by Pang et al. and to investigate the suitability of our shock tube facility for experiments in highly dilute conditions. Figure 4 shows a representative experimental OH trace from a TBHP decomposition experiment. The modified JetSurF mechanism was used to fit the measured OH traces over 755 – 989 K and 1.2 – 1.6 bar to obtain the following Arrhenius expression for $k_2$:

$$k_2 = 8.43 \times 10^{13} \exp\left(-\frac{18649}{T}\right) \text{s}^{-1}$$

(3)

Fig. 4. Measured OH mole fraction trace for TBHP decomposition. Overlaid are simulation results using the JetSurF mechanism along with perturbations of ±20%. Conditions: $T = 755$ K, $P = 1.52$ bar, 33.5 ppm TBHP / 50.3 ppm H$_2$O / Ar (bath gas).

Figure 5 shows a comparison between this rate expression and that of Pang et al.$^{13}$ where a similar experimental methodology was employed. Our measured activation energy is slightly higher than that of Pang et al.$^{13}$ resulting in about a 30% higher value of the rate constant close to
1000 K. The deviation between the two rate expressions decreases at lower temperatures with almost identical values near 700 K. Our measured results are therefore consistent with the reported uncertainty of ± 30% by Pang et al\textsuperscript{13}. Moreover, it should be noted that the effect of $k_2$ on the $\text{CO}_2$ sensitivity in CO/TBHP/Ar experiments decreases with increasing temperature, and, therefore, the deviation in $k_2$ close to 1000 K is not expected to have a large effect on the determination of $k_1a$.

![Fig. 5. Comparison of the TBHP decomposition rate between this work and Pang et al.\textsuperscript{13}](image)

3.3 CO + OH Rate Measurements

The CO + OH rate was measured under pseudo-first order reaction conditions where the TBHP concentration was nominally kept between 100 – 150 ppm and CO in excess at 0.5%. This led to the $\text{CO}_2$ concentration profile being sensitive to $k_1a$, as exemplified by Fig. 3. Measurements were conducted over conditions (700 – 1230 K and 1.2 – 9.8 bar) not covered by previous shock tube studies. Figure 6 shows a representative $\text{CO}_2$ trace at 1.43 atm for a mixture of 116 ppm TBHP / 174 ppm H$_2$O / 0.5% CO / Ar. The ±20% perturbations illustrate the
sensitivity of the measured CO$_2$ profiles to the target reaction rate. The measured rate constants are plotted in Fig. 7 in Arrhenius form for the three pressure ranges investigated here. Due to the relatively narrow temperature range investigated in this study, the results for each pressure range can be fitted to a simple Arrhenius expression. The respective Arrhenius expressions for the three pressure ranges are given as follows (including fitting errors):

\[
k_{1a}(1.2 - 1.6 \text{ bar}) = (9.14 \pm 2.17) \times 10^{-13} \exp\left(-\frac{(1265 \pm 190)}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[
k_{1a}(4.3 - 5.1 \text{ bar}) = (8.70 \pm 0.84) \times 10^{-13} \exp\left(-\frac{(1156 \pm 83)}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

\[
k_{1a}(9.6 - 9.8 \text{ bar}) = (7.48 \pm 1.92) \times 10^{-13} \exp\left(-\frac{(929 \pm 192)}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

Fig. 6. Measured CO$_2$ mole fraction trace overlaid with simulation results using the JetSurF mechanism along with perturbations of ±20%. Conditions: T = 962 K, P = 1.45 bar, 116 ppm TBHP / 174 ppm H$_2$O / 0.5% CO / Ar (bath gas).
The expression for the low-pressure limit given by Joshi and Wang\textsuperscript{4} suggests that the pressure range used in the current study is near the low-pressure limit. However, as illustrated by Fig. 7, the measured rate constant is slightly pressure dependent. This is even more prominent in Fig. 8 where interpolated rate constant values at 819 K are plotted against the total number density. The pressure dependence of $k_1$ has been evaluated in recent works via master equation modeling by Joshi and Wang\textsuperscript{4} and by Weston et al.\textsuperscript{5} at selected temperatures for comparison with experimental results of Fulle et al.\textsuperscript{10} Figure 8 shows such a comparison at 819 K wherein experimental data points other than those by Fulle et al.\textsuperscript{10} are interpolated results. The calculated low-pressure limit rate constant differs by approximately 22\% between the modeling results of Wang and Weston et al.\textsuperscript{4-5} The data points from the current work are found to be lower than both of these calculations albeit being closer to Joshi and Wang\textsuperscript{4}. 

![Fig. 7. Measured rate constants and Arrhenius fits for $k_{1a}$.](image)
Fig. 8. Pressure dependence of $k_1$ at 819 K including results from experiments\textsuperscript{10-12} and master
equation modeling\textsuperscript{4-5}.

Based on the expression for the low-pressure limit given by Joshi and Wang (Eq. 22 in
Ref 4) and the results from Fig. 8, the measured rate constants for the pressure range 1.2 – 1.6
bar can be assumed to be at the low-pressure limit for comparison purposes. Figure 9 shows the
measured low-pressure data from this work compared with flow reactor results by Westenberg et
al.\textsuperscript{9} and Ravishankara et al.\textsuperscript{11} and shock tube measurements by Wooldridge and Hanson\textsuperscript{8}. Also
shown are the theoretical results by Joshi and Wang\textsuperscript{4}. The fit to the current work is found to be
lower than most of the literature measurements and systematically lower than the calculation by
Joshi and Wang by 30% or more. This difference can be attributed to two main factors: the
choice of the OH precursor and the sensitivity of the detection technique. The OH precursor used
in this work (TBHP) has well-characterized secondary chemistry and can be used in highly dilute
conditions, as opposed to previous works involving less efficient OH production methods. The
detection technique for CO$_2$ employed in this study has been shown to be relatively free from
interference from secondary effects and is highly quantitative as opposed to the relatively
broadband techniques used for OH in previous works.
Fig. 9. Arrhenius plot for \( k_1 \) at the low-pressure limit from literature\(^4,8-9,11\) and the current data for the pressure range 1.2-1.6 bar.

4. Uncertainty in Rate Measurements

Major sources of uncertainty in \( k_{1a} \) are given in Table 1 for a representative low temperature case. Other cases at the extremes of the conditions used in this work can be found in the Supplementary Material. The individual uncertainty contributions to the final rate were determined by applying the listed perturbations and re-fitting the rate constant through kinetic simulations. The most significant contribution to the overall uncertainty is from the TBHP decomposition rate \( k_2 \) because the sensitivity to \( k_2 \) is more significant at lower temperatures. As stated previously, the uncertainty in \( k_2 \) is taken to be the same as that by Pang et al.\(^{13}\), i.e., \( \pm 30\% \).

Uncertainties associated with the \( \text{CO}_2 \) diagnostic arise from uncertainty in the absorption coefficient and noise in the detection system. The uncertainty in initial TBHP concentration is taken to be the maximum variation in measured peak OH mole fractions for high-temperature cases, i.e., \( \pm 10\% \). The \( \text{H}_2\text{O} \) concentration in the reactive system did not have a significant effect on the uncertainty, as found by Pang et al.\(^{13}\) for similar conditions. While the uncertainty in the
reflected shock temperature is found to have an effect on the overall uncertainty, the uncertainty in reflected shock pressure has negligible influence on the measured rate constant. Moreover, the effect of vibrational relaxation of CO is also negligible due to equilibrium population of CO being overwhelmingly in the ground state at these temperatures, as was noted by Wooldridge and Hanson.

Table 1. Major sources of uncertainty in $k_{1a}$ for $T=862$ K, $P=1.52$ bar, 120 ppm TBHP / 180 ppm H$_2$O / 0.5 % CO / Ar (bath gas).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncertainty</th>
<th>Effect on $k_{1a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBHP Decomposition Rate, $k_2$</td>
<td>30%</td>
<td>14.6%</td>
</tr>
<tr>
<td>CO$_2$ Diagnostic</td>
<td>5%</td>
<td>6.92%</td>
</tr>
<tr>
<td>Initial TBHP concentration</td>
<td>10%</td>
<td>4.62%</td>
</tr>
<tr>
<td>Reflected Shock Temperature, T</td>
<td>1%</td>
<td>3.85%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>17.3%</strong></td>
</tr>
</tbody>
</table>

5. Conclusions

Rate constants for the CO + OH reaction have been measured near the low-pressure limit for temperature of interest to low-temperature combustion. Compared to previous theoretical determinations, the measured rate constants have been found to be systematically lower for these conditions. The calculated low-pressure limit rate constant by Joshi and Wang is found to be closest to our measurements. The low detection limit of the CO$_2$ diagnostic used in this work allows for a more accurate determination of the rate constant at these conditions leading to lower uncertainties in the modeling of low-temperature combustion phenomena.
Acknowledgments

The research reported in this publication was supported by funding from King Abdullah University of Science and Technology (KAUST).

References


TOC Graphic: