Assessment of Current Chemiluminescence Kinetics Models at Engine Conditions

Chemiluminescence continues to be of interest as a cost-effective optical diagnostic for gas turbine combustor health monitoring. However, most chemical kinetics mechanisms of the chemiluminescence of target species such as OH*, CH*, and CO2 were developed from atmospheric-pressure data. The present paper presents a study wherein the ability of current kinetics models to predict the chemiluminescence trends at engine pressures was assessed. Shock-tube experiments were performed in highly diluted mixtures of H2/O2/Ar at a wide range of pressures to evaluate the ability of a current kinetics model to predict the measured trends. At elevated pressures up to 15 atm, the currently used reaction rate of $H + O + M = OH^* + M$ (i.e., without any pressure dependence) significantly overpredicts the amount of OH* formed. Other important chemiluminescence species include CH* and CO2, and separate experiments were performed to assess the validity of existing chemical kinetics mechanisms for both of these species at elevated pressures. A pressure excursion using methane-oxygen mixtures highly diluted in argon was performed up to about 15 atm, and the time histories of CH* and CO2 were measured over a range of temperatures from about 1700 to 2300 K. It was found that the existing CH* mechanism captured the T and P trends rather well, but the CO2* mechanism did a poor job of capturing both the temperature and pressure behavior. With respect to the modeling of collider species, it was found that the current OH* model performs well for N2, but some improvements can be made for CO2. [DOI: 10.1115/1.4004735]

Introduction

The goal of the present study was to broaden the understanding of the chemical kinetics of species used in gas turbine applications for their chemiluminescence light intensities. Such efforts have been described in [1]. Making quantitative measurements of chemiluminescence species concentrations or even relative concentrations requires knowledge of the chemical kinetics of the molecules of interest. These species include OH*, CH*, CO2*, and C2*. Because of their small concentrations in the combustion zone (several orders of magnitude less than their ground-state counterparts), absolute measurements of the concentrations of the excited species are difficult. A shock tube is one way to produce the high temperatures seen in a gas turbine combustion zone, and it can be used as a model device for producing controlled conditions for obtaining time histories of excited species for kinetics model validation. Shock-tube experiments can also be used to obtain specific rate coefficients of key reactions in the formation and deactivation of the excited species.

The present paper is concerned mainly with the assessment of and eventual improvement to the kinetics models for OH*, CO2*, and CH* chemiluminescence. The work can be divided into the three parts: (1) OH* chemiluminescence at elevated pressure; (2) pressure effects on CH* and CO2* chemiluminescence; and (3) the effect of various collider species ($M = CO_2, N_2$) on OH* chemiluminescence. The following sections are divided into the same three parts, following a brief section on the experimental setup. Further details on the OH* results are in the thesis by Donato [2].

Experimental Setup

All experiments were performed in the shock-tube facility described by Aul [3]. This facility contains a 4.72-m driven section with a 1.524-m internal diameter and a 4.92-m driver section with a 7.62-cm inner diameter. The inner diameter of the driver section is then expanded through a diverging section to the driven diameter directly after the diaphragm location. The shock tube is made of 304 stainless steel. For every test, helium was used as the driver gas, and polycarbonate diaphragms were used for the highest-pressure experiments. High-purity gases were used to make the mixtures, which were all highly diluted in ultrahigh purity (UHP) argon (99.9995%). The oxygen and hydrogen were both UHP grade, and the methane was research grade (99.95%). The incident-shock velocity at the test region was found using five pressure transducers (PCB 113) set in series along the side of the shock tube which send signals to 4 Fluke PM 6666 time-interval counters. The incident-shock velocity was used with the standard one-dimensional shock relations to determine the conditions behind the reflected shock wave for each experiment.

Light emission from the chemiluminescence of OH*, CH*, or CO2 was collected through two CaF2 windows located at a sidewall location 1.0 cm from the endwall. For the CH* and CO2* measurements, both emission signals were recorded simultaneously since the two windows were located on opposite sides of the driven tube. Two Hamamatsu 1P21 photomultiplier tubes (PMT) in custom-made enclosures were used to measure the emission through narrowband filters. Further details on the filter wavelengths and calibration of the optical setup are provided below.

OH* Chemiluminescence. These experiments focused on shock-tube mixtures of hydrogen and oxygen highly diluted in argon to isolate the contribution of the pressure-dependent reaction

$$H + O + M \rightarrow OH^* + M$$

to the formation of OH* (i.e., only H and O atoms available, with no hydrocarbons). We chose mixtures that had been used in prior experiments by the primary authors [4,5]. Once the optimal settings were obtained and experiments underway, it was necessary

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to validate the results with other data available in the literature. Petersen et al. [4] performed shock-tube experiments using the same mixture of $H_2/O_2/Ar$ with 98.5% dilution, $\phi = 1.0$, to examine the chemical kinetics of $OH^*$ ($A^3Σ^+-X^2Σ^+$) chemiluminescence in the temperature range from 1010 to 1750 K at low pressure. The shock tube used in the study by Petersen et al. [4] is similar to the one used in this study and is detailed in [5]. Since the optical settings differ between sets of experiments, it is necessary to normalize the data to a particular temperature and pressure; thus enabling a direct comparison of the data. A set of data was taken with the current setup to compare directly with the earlier data, and Fig. 1 verifies the repeatability of the low-pressure experimental results obtained by Petersen and co-workers.

Additionally, the experimentally obtained $OH^*$ profiles of this study were also compared to those of Petersen et al. [4] for cases of similar temperature. Figure 2 shows general agreement in the shape of the profiles between experiments. Slight differences can be attributed to the difference in temperature and pressure; thus enabling a direct comparison of the data. A set of data was taken with the current setup to compare directly with the earlier data, and Fig. 1 verifies the repeatability of the low-pressure experimental results obtained by Petersen and co-workers.

Finally, high-pressure experiments were performed at 10 and 15 atm over a wide range of temperatures. Comparisons of the experimental results to the $OH^*$ model of Hall and Petersen [5] are shown in Fig. 3. Note that the base kinetics model for the $H_2-O_2$ chemistry is from the GRI 3.0 mechanism, and the simulations were performed using Chemkin [6]. Error bars are shown in Fig. 3 to represent the uncertainty in the value of the peak magnitude due to experimental repeatability from test to test, and was determined to be 10%. An uncertainty of ±10 K is associated with the experimental temperature determination. Although the model does a good job of predicting peak $OH^*$ formation at atmospheric pressure as expected, it significantly overpredicts the peak concentration at higher pressures (10 and 15 atm). The model also shows a different trend than the data at the highest temperatures by predicting a decrease in peak $OH^*$. In ongoing work, the experimental data in Fig. 3 and more like it are being used to obtain an improved model at elevated pressures.

**CO$_2^*$ and CH* Chemiluminescence.** Shock-tube experiments were performed in an argon-diluted methane/oxygen mixture to examine $CO_2^*$ and CH* at elevated pressures. $CO_2^*$ emission was captured using a narrow bandpass interference filter at $337 \pm 2$ nm, while CH* emission was captured at $430 \pm 5$ nm, as shown in Fig. 4. Capturing the broadband emission of $CO_2^*$ with a 4-nm bandpass filter is adequate since any portion of the spectrum should be due to the excited state of $CO_2$; that is, a measurement focused at 400 nm should give time-specific results similar to those at $337$ nm, just at a higher overall intensity.
The overall chemiluminescence reaction for \( \text{CO}_2^* \) is given by
\[
\text{CO} + \text{O} \rightleftharpoons \text{CO}_2 + h\nu
\]  
where the chemiluminescence intensity \( I \) is
\[
I = I_o [\text{CO}] [\text{O}]
\]
The formation and depletion of \( \text{CO}_2^* \) can be shown by the following three steps:
\[
\text{CO} + \text{O} + \text{M} \rightleftharpoons \text{CO}_2^* + \text{M}
\]
\[
\text{CO}_2^* \rightleftharpoons \text{CO}_2 + h\nu
\]
\[
\text{CO}_2 + \text{M} \rightleftharpoons \text{CO}_2 + \text{M}
\]
These reactions yield a rate coefficient \( I_o = (K_1 K_2)/K_o \). To date, there exists no detailed \( \text{CO}_2^* \) mechanism. Rather, the photon emission rate \( i_{\text{CO}_2^*} \) is given by a global rate that is dependent on the concentrations of [CO] and [O]. This global rate is given by Slack et al. [8] and recently used by Nori and Seitzman [9] as
\[
i_{\text{CO}_2^*} = 3.3(\pm0.3) \times 10^5 \exp(-2300/T)[\text{CO}][\text{O}]
\]
where temperature is in K, and species concentrations are in units of mol/cm\(^3\).

The detailed mechanism used to model CH* was taken from de Vries et al. [10], where CH* is formed by the following reactions:
\[
\text{C}_2\text{H} + \text{O} \rightleftharpoons \text{CO} + \text{CH}^*
\]
\[
\text{C}_3 + \text{OH} \rightleftharpoons \text{CO} + \text{CH}^*
\]
\[
\text{C} + \text{H} + \text{M} \rightleftharpoons \text{CH}^* + \text{M}
\]
The depletion of CH* occurs by way of the following reactions:
\[
\text{CH}^* \rightleftharpoons \text{CH} + h\nu
\]
\[
\text{CH}^* + \text{M} \rightleftharpoons \text{CH} + \text{M}
\]
Future experiments are planned to determine the rate coefficient for this reaction and a better overall chemical kinetics model for \( \text{CO}_2^* \). There is also the possibility of additional pathways for \( \text{CO}_2^* \) formation that are not considered in the crude and virtually untested \( \text{CO}_2^* \) mechanism employed herein. Some possibilities might include reactions where CO acts as a third body and bimolecular collisions that could be energetic enough to excite \( \text{CO}_2 \) to \( \text{CO}_2^* \).

**Effect of Collider Species.** A separate series of experiments was conducted to determine how well the OH* model performed when collider species other than argon were present in significant quantities. Two mixtures were utilized for this part of the study. The first mixture was a stoichiometric \( \text{H}_2\text{O}_2 \) mixture in a nitrogen bath gas with 97% by volume \( \text{N}_2 \). The second mixture contained \( \text{CO}_2 \) in the following blend: 0.006 \( \text{H}_2 + 0.003 \text{ O}_2 + 0.05 \text{ CO}_2 + 0.941 \text{ Ar} \). Note that a test mixture containing only carbon dioxide as the bath gas species is not practical in a reflected-shock experiment due to the nonideal effects that would exist with the mostly triatomic mixture [11].

Figure 9 shows two examples of OH* time histories for the \( \text{N}_2 \) bath gas, one at 1208 K and the other at 1272 K, both at a pressure of 1.1 atm. In both cases seen in Fig. 9, the model does a good job at predicting the rise and decay of the OH* concentration at this low-pressure condition. There is a slight overprediction of the decay by the model which is almost within the signal-to-noise of the data trace. Therefore, there could be room for slight improvements in the \( \text{N}_2 \) collider kinetics, but the current performance is probably acceptable for most applications.
inadequacies of the high-pressure OH* chemistry highlighted in Fig. 3, pressures higher than about 1 atm were not included in this collider species study.

The repeatability of the nitrogen-bath experiments was quite good, as seen in Fig. 10 for two different tests at nearly the same temperatures (1183 and 1176 K). For the entire series of experiments with the 97% N2 mixture between about 1070 and 1270 K, the peak concentration of OH* can be compared. Figure 11 shows the peak OH* concentration normalized to the concentration obtained at 1272 K for both the experiment and the model. Both sets of points in Fig. 11 are in fair agreement, indicating that the kinetics model does an adequate job at predicting the behavior with nitrogen as the collider species.

Comparisons between model and experiment for the mixture containing CO2 are shown in Figs. 12 and 13 for the OH* time history and peak concentration, respectively. As seen in Fig. 12 for the representative OH* time history, the model tends to over-predict the decay rate of OH* relative to the measured results,

Fig. 5 Representative profiles from stoichiometric methane/oxygen mixtures in 99.1% Ar are compared to model profiles for CO2 and CH*. Calculations are adjusted in time so that the times of peak concentration coincide with the measured results. (a) CO2 profiles at P = 1.2 atm. (b) CH* profiles at P = 1.2 atm. (c) CO2 profiles at P = 14.3 atm. (d) CH* profiles at P = 14.3 atm.

Fig. 6 The product of the CO concentration times the O concentration dictates the overall profile shape of CO2*. Results here are calculated from the kinetics model (GRI 3.0) for the stoichiometric CH4-O2 mixture in 99.1% Ar. (a) CO2* profiles at P = 1.2 atm. (b) CH* profiles at P = 14.3 atm.
indicating that some improvement in the model with respect to CO₂ as a collider species can be made in the future. However, when comparing the peak OH⁺ concentration over the measured range of temperatures (about 1300 to 2200 K), the model seems to perform fairly well (Fig. 13) but overpredicts the peak concentration near 1500 K and under predicts it for temperatures above about 1900 K. A detailed sensitivity analysis would shed more insight into the discrepancies seen in Fig. 13 and should therefore be performed in the follow-up work to the present study.

Finally, it is of interest to compare the temperature trends observed using the peak level of OH⁺ to the trends observed when the full width of the concentration history is utilized. Figure 14 shows the comparison between the normalized peak values to the normalized areas under the profiles of OH⁺ time histories calculated using the model. One can infer from Fig. 14 that the same temperature trend is observed whether the peak or full area of the OH⁺ is used, at least for the range of conditions measured herein for the lower-pressure cases near 1 atm.
Shock-tube experiments and kinetics modeling were performed to assess the chemiluminescence kinetics of \( \text{OH}^* \), \( \text{CO}_2^* \), and \( \text{CH}^* \) at gas turbine pressures and temperatures. In the first part, the pressure dependence of the key \( \text{OH}^* \) formation reaction \( \text{O} + \text{H} + \text{M} \rightarrow \text{OH}^* + \text{M} \) was assessed at pressures up to 14 atm using \( \text{H}_2-\text{O}_2 \) mixtures highly diluted in argon. These measurements involved a careful set of experiments that utilized a calibration based on the assumed kinetics of \( \text{OH}^* \) at 1 atm. A second set of experiments was performed to assess the kinetics models of \( \text{CO}_2^* \) and \( \text{CH}^* \) at elevated pressures. The results of this pressure excursion using methane-oxygen mixtures in argon was that the \( \text{CH}^* \) mechanism is good at capturing the temperature and pressure trends, while the \( \text{CO}_2^* \) model is as defined herein rather poor. Finally, measurements utilizing mixtures containing large levels of \( \text{N}_2 \) or \( \text{CO}_2 \) were performed, and it was found that the model does a good job with nitrogen species at the conditions studied (1 atm) for \( \text{OH}^* \). For the mixture containing \( \text{CO}_2 \), some improvements are warranted since the model tends to overpredict the decay rate of \( \text{OH}^* \).

Summary

Shock-tube experiments and kinetics modeling were performed to assess the chemiluminescence kinetics of \( \text{OH}^* \), \( \text{CO}_2^* \), and \( \text{CH}^* \) at gas turbine pressures and temperatures. In the first part, the pressure dependence of the key \( \text{OH}^* \) formation reaction \( \text{O} + \text{H} + \text{M} \rightarrow \text{OH}^* + \text{M} \) was assessed at pressures up to 14 atm using \( \text{H}_2-\text{O}_2 \) mixtures highly diluted in argon. These measurements involved a careful set of experiments that utilized a calibration based on the assumed kinetics of \( \text{OH}^* \) at 1 atm. A second set of experiments was performed to assess the kinetics models of \( \text{CO}_2^* \) and \( \text{CH}^* \) at elevated pressures. The results of this pressure excursion using methane-oxygen mixtures in argon was that the \( \text{CH}^* \) mechanism is good at capturing the temperature and pressure trends, while the \( \text{CO}_2^* \) model is as defined herein rather poor. Finally, measurements utilizing mixtures containing large levels of \( \text{N}_2 \) or \( \text{CO}_2 \) were performed, and it was found that the model does a good job with nitrogen species at the conditions studied (1 atm) for \( \text{OH}^* \). For the mixture containing \( \text{CO}_2 \), some improvements are warranted since the model tends to overpredict the decay rate of \( \text{OH}^* \).

One can conclude from this study that improvements should be made to the \( \text{CO}_2^* \) mechanism, including its pressure dependence.
via the reaction CO + O + M ⇌ CO₂ + M, as well as an assessment of whether additional reactions are needed. A similar conclusion can be drawn for the OH* pressure dependence, and further work should be done to assess the validity of the OH* mechanism in the presence of hydrocarbons at elevated pressures. In future work, the effect of collider species N₂ and CO₂ (and perhaps H₂O) on the kinetics of CH* and CO₂* should also be assessed.

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**References**


