RATE DETERMINATION OF THE CO$_2^*$ CHEMILUMINESCENCE REACTION

CO + O + M = CO$_2^*$ + M

A Thesis

by

MADELEINE MARISSA KOPP

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Approved by:

Chair of Committee, Eric L. Petersen
Committee Members, Rodney D. W. Bowersox
David A. Staack
Head of Department, Jerald A. Caton

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ABSTRACT

The use of chemiluminescence measurements to monitor a range of combustion processes has been a popular area of study due to their reliable and cost-effective nature. Electronically excited carbon dioxide (CO$_2^*$) is known for its broadband emission, and its detection can lead to valuable information; however, due to its broadband characteristics, CO$_2^*$ is difficult to isolate experimentally, and the chemical kinetics of this species is not well known. Although numerous works have monitored CO$_2^*$ chemiluminescence, a full kinetic scheme for the species has yet to be developed.

A series of shock-tube experiments was performed in H$_2$-N$_2$O-CO mixtures highly diluted in argon at conditions where emission from CO$_2^*$ could be isolated and monitored. These results were used to evaluate the kinetics of CO$_2^*$, in particular, the main CO$_2^*$ formation reaction, CO + O + M \rightleftharpoons CO$_2^*$ + M (R1). Based on collision theory, the quenching chemistry of CO$_2^*$ was determined for eleven common collision partners. The final mechanism developed for CO$_2^*$ consisted of 14 reactions and 13 species. The rate for R1 was determined based on low-pressure experiments performed in two different H$_2$-N$_2$O-CO-Ar mixtures.

Final mechanism predictions were compared with the experimental results at low and high pressures, with good agreement seen at both conditions. Peak CO$_2^*$ trends with temperature as well as overall CO$_2^*$ species time histories were both monitored. Comparisons were also made with previous experiments in methane-oxygen mixtures, where there was slight over-prediction of CO$_2^*$ experimental trends by the mechanism.
Experimental results and mechanism predictions were also compared with past literature rates for CO$_2^*$, with good agreement for peak CO$_2^*$ trends, and slight discrepancies in overall CO$_2^*$ species time histories. Overall, the ability of the CO$_2^*$ mechanism developed in this work to reproduce a range of experimental trends represents an improvement over existing models.
ACKNOWLEDGMENTS

I would like to first and foremost thank my advisor and committee chair, Dr. Petersen, for his exceptional guidance throughout my research experience both as an undergraduate and graduate student. Thanks also go out to my committee members, Dr. Bowersox and Dr. Staack, for their help and support in serving on my committee.

I also owe gratitude to my co-workers, who have helped tremendously in making this work possible. Special thanks go out to Dr. Olivier Mathieu for his help in running experiments, as well as to Marissa Brower, for her work in the initial stages of the project. Finally, I would like to acknowledge my family, whose moral support has been a tremendous source of encouragement and perseverance.
NOMENCLATURE

[X] Molar concentration of species X

ν Fundamental frequency

k Reaction rate coefficient

A Pre-exponential factor

n Temperature exponent

Ea Activation energy

R Universal gas constant

N Number of moles

HR Heat of reaction

h Planck’s constant

c Speed of light

λ Wavelength of chemiluminescence transition

NA Avogadro’s number

cp Constant pressure specific heat

H° Enthalpy

S° Entropy

ΔHf Enthalpy of formation

Z Collision frequency
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$\sigma_{AB}$</td>
<td>Mean collision diameter of molecules A and B</td>
</tr>
<tr>
<td>$k_b$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$\mu_{AB}$</td>
<td>Reduced mass of molecules A and B</td>
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</table>
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>NOMENCLATURE</td>
<td>v</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
</tr>
<tr>
<td>CHAPTER I INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER II LITERATURE REVIEW AND BACKGROUND</td>
<td>4</td>
</tr>
<tr>
<td>Literature Review</td>
<td>4</td>
</tr>
<tr>
<td>Kinetics Theory</td>
<td>8</td>
</tr>
<tr>
<td>CO₂* Reaction Kinetics</td>
<td>8</td>
</tr>
<tr>
<td>Quenching Theory</td>
<td>12</td>
</tr>
<tr>
<td>CHAPTER III EXPERIMENTAL SETUP AND MODELING</td>
<td>14</td>
</tr>
<tr>
<td>Shock-Tube Experimental Setup</td>
<td>14</td>
</tr>
<tr>
<td>Chemical Kinetics Modeling</td>
<td>15</td>
</tr>
<tr>
<td>Experimental Conditions</td>
<td>16</td>
</tr>
<tr>
<td>Fitting Scheme</td>
<td>18</td>
</tr>
<tr>
<td>CHAPTER IV RESULTS AND DISCUSSION</td>
<td>28</td>
</tr>
<tr>
<td>Temperature Dependence of Peak Magnitude</td>
<td>28</td>
</tr>
<tr>
<td>Species Time Histories</td>
<td>30</td>
</tr>
<tr>
<td>Uncertainty</td>
<td>32</td>
</tr>
<tr>
<td>Comparisons with Past Works</td>
<td>37</td>
</tr>
<tr>
<td>High-Pressure Excursion</td>
<td>44</td>
</tr>
<tr>
<td>CHAPTER V CONCLUSIONS AND RECOMMENDATIONS</td>
<td>46</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>48</td>
</tr>
</tbody>
</table>

vii
LIST OF FIGURES

Figure 1. Recreation of a portion of the chemiluminescence spectrum showing the broadband background of the chemiluminescence from CO₂*, HCO*, and CH₂O*, based on work from [4, 5, 8, 32, 33]. ......................................................... 2

Figure 2. Model predictions for various chemiluminescence species in 0.0005H₂ + 0.01N₂O + 0.03CO + 0.9595Ar at 1936 K and 1.5 atm. Profiles are normalized to peak values. .................................................................................. 17

Figure 3. Experimental CO₂* time history showing PMT output in mV as a function of time in microseconds at 1700 K and 1.6 atm in Mix 1. .................. 19

Figure 4. Peak CO₂* normalized to 2202 K for experiments in Mix 0 at an average pressure of 1.4 atm. ........................................................................ 20

Figure 5. Peak CO₂* mechanism predictions with experimental data from Mix 0 using the ground-state rate for R1. ......................................................... 21

Figure 6. CO₂* sensitivity and rate of production analysis at 1936 K and 1.5 atm for Mix 0 (a), (c) and Mix 1 (b), (d). .......................................................... 22

Figure 7. Normalized peak CO₂* from experiments compared with final mechanism predictions for Mix 0 (a) and Mix 1 (b). ......................................................... 29

Figure 8. Normalized CO₂* experimental profiles compared with the final mechanism predictions for low, medium, and high temperature in Mix 0 (a), (c), (e) and Mix 1 (b), (d), (f). .................................................................................... 30

Figure 9. Effect of changes to CO₂ + Ar ⇌ CO₂ + Ar (R3) on mechanism predictions compared to normalized CO₂* peak trends from experiments in Mix 0 (a) and Mix 1 (b). ................................................................. 33

Figure 10. Effect of changes to N₂O(+M) ⇌ N₂ + O(+M) (R15) on mechanism predictions compared to normalized CO₂* peak trends from experiments in Mix 0 (a) and Mix 1 (b). ................................................................. 35

Figure 11. Effect of changes to CO + OH ⇌ CO₂ + H (R16) on mechanism predictions compared to normalized CO₂* peak trends from experiments in Mix 0 (a) and Mix 1 (b). ................................................................. 36

Figure 12. Effect of omitting the efficiency factors for CO + O + M ⇌ CO₂ + M (R1) and omitting HCO + O ⇌ CO₂ + H (R2) on mechanism predictions
compared to normalized CO$_2^*$ peak trends from experiments in Mix 0 (a) and Mix 1 (b).

Figure 13. Normalized peak CO$_2^*$ from experiments by Petersen et al. [9] in a stoichiometric mixture of methane and oxygen highly diluted in argon at an average pressure of 1.3 atm compared with mechanism predictions from this work.

Figure 14. Normalized CO$_2^*$ experimental profile at 2092 K and 1.2 atm from [9] compared with the mechanism prediction from this work.

Figure 15. Normalized peak CO$_2^*$ from experiments compared with mechanism predictions from this work, Slack and Grillo [58], and Sulzmann et al. [40] for Mix 0 (a) and Mix 1 (b).

Figure 16. Normalized CO$_2^*$ experimental profiles compared with mechanism predictions from this work, Slack and Grillo [58], and Sulzmann et al. [40] at 1936 K and 1.5 atm in Mix 0 (a) and 1927 K and 1.5 atm in Mix 1 (b).

Figure 17. Termolecular rate constants for R1 from Sulzmann et al. and this work plotted against inverse temperature.

Figure 18. Normalized peak CO$_2^*$ from experiments in Mix 0 at an average pressure of 10.5 atm compared with mechanism predictions from this work.

Figure 19. Normalized CO$_2^*$ experimental profiles compared with final mechanism predictions at 1654 K and 10.6 atm (a) and 2176 K and 10.5 atm (b).
LIST OF TABLES

Table 1. Reaction mechanism for CO$_2$*. Units are cal, cm, mole, sec, K. .......................... 10

Table 2. Molecular parameters used in the hard-sphere calculations for CO$_2$* quenching reactions, taken from Turns [75]. ................................................................. 13

Table 3. Mixture compositions for Mix 0 and Mix 1, in % volume. ................................. 18

Table 4. Experimental conditions for Mix 0 and Mix 1 in terms of average pressures and temperature range. ........................................................................................................ 18

Table 5. Temperature, pressure, and peak CO$_2$* signal from the experiments used to determine R1. .............................................................................................................. 28
CHAPTER I
INTRODUCTION

Chemiluminescence has proven to be a significant diagnostic tool for combustion health monitoring. Its relative simplicity and non-intrusive nature make it ideal for a variety of applications such as heat release sensing [1-6], equivalence ratio detection [5-8], and fuel consumption rate monitoring [4].

Chemiluminescence describes the process in which a molecule transitions from an excited state to its ground state, causing a release of energy in the form of light. Common excited state species that have been studied are OH* [6, 9-27], CH* [6, 8, 9, 21, 28-30], NH* [21, 28, 30], and NO* [29, 31], among others. A crucial aspect in the study of chemiluminescence is the ability of chemical kinetics mechanisms to predict measured trends. The chemistry of OH* and CH*(A) is the most well-known, and their detection is easily accessible due to their sharp emission features near 307 nm and 431 nm, respectively, as shown in Figure 1. However, the chemistry of other species such as CO₂*, HCO*, and CH₂O*, also shown in Figure 1, is less well-known due in part to the fact that their emission features are more broadband in nature, so they are difficult to isolate experimentally.
Figure 1. Recreation of a portion of the chemiluminescence spectrum showing the broadband background of the chemiluminescence from CO$_2^*$, HCO*, and CH$_2$O*, based on work from [4, 5, 8, 32, 33].

Much of the broadband background emission in hydrocarbon flames has been attributed to emission from CO$_2^*$ [1, 4, 5, 33-47], but the various proposed kinetics mechanisms for CO$_2^*$ [4, 8, 35, 36, 40, 48-59] are not in complete consensus. It has been identified by Broida and Gaydon [60] and Laidler and Shuler [59] that the main reaction that goes to forming CO$_2^*$ is

$$CO + O + M \rightarrow CO_2^* + M$$  \hspace{1cm} R1

However, the rate for this reaction is still up for debate [40, 48, 61], and there is discrepancy as to the overall order of this reaction as well [48, 53, 57, 59, 62]. Although several works have made measurements of CO$_2^*$ chemiluminescence [1-5, 8, 9, 34-38,
most have been geared toward determining the rate of the CO\textsubscript{2} radiative recombination [38, 42, 50-54, 58, 60, 63, 68]:

\[ CO + O \rightleftharpoons CO\textsubscript{2} + h\nu \]

Due to the lack of consensus on CO\textsubscript{2}* chemiluminescence chemistry in general, the goal of this study was to formulate a complete kinetics scheme for the formation and depletion of CO\textsubscript{2}* and determine the rate of the title reaction, R1, using a combination of fundamental kinetics theory as well as a fitting scheme to experimental data. This thesis provides an overview of the existing contributing works available in the literature as well as a brief background and review of kinetics theory in Chapter II. In Chapter III, the experimental apparatus and chemical kinetics modeling are described, and the experimental conditions of the study are presented. Chapter III also includes the rate-determining process for R1. The results are presented in Chapter IV along with an uncertainty analysis on the proposed kinetics scheme. Comparisons with alternate kinetic schemes and a high-pressure excursion are also presented in Chapter IV. Finally, Chapter V provides conclusions and identifies future avenues of research for continuation of this work.
CHAPTER II
LITERATURE REVIEW AND BACKGROUND

Literature Review

Chemiluminescence from electronically excited CO\textsubscript{2} (herein denoted at CO\textsubscript{2}*) consists of a broad continuum that can extend from below 300 nm to above 600 nm [1, 4, 33-43, 59] along with discrete CO flame bands [35, 36, 41, 42, 48, 59, 60, 68, 70]. While the continuum is more prominent at high temperatures (above 1000 K) [35, 36], the flame bands are known to be favored at lower temperatures [35, 36, 42, 70]. The blue radiation observed in carbon monoxide flames is also said to come from CO\textsubscript{2}* emission [35, 38, 42, 50, 60].

Despite the extensive amount of work addressing CO\textsubscript{2}* chemiluminescence, its full chemical kinetics mechanism is still under debate. Because of its broadband nature, CO\textsubscript{2}* is difficult to isolate experimentally, so verification of the kinetics mechanism is challenging. Rather than using a full kinetics mechanism for CO\textsubscript{2}*, many studies have relied on the fact that CO\textsubscript{2}* chemiluminescence is proportional to the product of the concentrations of carbon monoxide and atomic oxygen [9, 35, 36, 38, 43, 47, 48, 52, 57, 58, 62, 63, 68, 73].

Studies of CO\textsubscript{2}* chemiluminescence have dated back to as early as the 1950’s. In 1951, Laidler and Shuler [59] studied gas-phase elementary reactions involving excited electronic states, in which CO\textsubscript{2}* emission was addressed. They attributed the carbon
dioxide continuum to the process $\text{CO} + \text{O} \rightarrow \text{CO}_2^* \rightarrow \text{CO}_2 + \hbar$ and identified R1 as a likely source for $\text{CO}_2^*$ in the carbon monoxide flame. Gordon and Knipe [49] investigated the kinetics of carbon monoxide and oxygen in 1955, and Kaskan [43] explored the source of the continuum in CO-H$_2$-air flames in 1959, concluding that the continuum accounts for approximately 95% of the radiation and suggesting that the light intensity should be proportional to the product of [CO] and [O].

A number of additional works on $\text{CO}_2^*$ were published in the 1960’s. In 1962, Clyne and Thrush [35] measured intensities of the chemiluminescent emission from $\text{CO}_2^*$ and NO$_2^*$ at low temperatures (200 – 300 K) and found that $\text{CO}_2^*$ emission occurs from below 300 nm to above 500 nm, with peak intensity around 400 nm. The kinetics of $\text{CO}_2^*$ were detailed in a later work by Clyne and Thrush [48] in 1963. Information on the carbon monoxide flame bands was presented by Dixon [70] in 1963, with an extensive discussion on the electronic structure and molecular configuration of CO$_2$ in its ground and excited states. Davies [36] studied carbon dioxide dissociation at high temperatures (6,000 – 11,000 K) behind reflected shock waves in 1965 and discussed the nature of the excited state of CO$_2$ at these conditions. In another shock-tube study by Myers [52] in 1967, a rate constant for the radiative recombination of carbon monoxide and oxygen was determined by recording emission intensity at six spectral intervals between 250 and 800 nm.

The 1970’s and 80’s saw a continued interest in the chemistry of $\text{CO}_2^*$, and a few works stand out. The exponential growth rate of $\text{CO}_2^*$ chemiluminescence was measured in shock-heated H$_2$-CO-O$_2$-Ar mixtures by Schott [56] in 1973, and in another
work by Schott et al. [38] in 1974, oxygen-atom yields were determined by monitoring CO$_2^*$ emission and using the relation that intensity is proportional to the concentration product of [CO] and [O], as was done by Jachimowski in 1974 [68]. Gaydon [42] identified CO$_2^*$ as the source of carbon monoxide flame bands and provided an extensive discussion on CO$_2^*$ emission and chemical kinetics in a 1976 text.

Several works dedicated to CO$_2^*$ chemiluminescence measurements were conducted in the 1980’s. In 1981, Pravilov and Smirnova [54] made room-temperature CO$_2^*$ chemiluminescence measurements in a small, homogeneous reactor, and in 1985, Slack and Grillo [58] made spectral measurements of CO$_2^*$ chemiluminescence between 260 and 700 nm at high temperatures (1300 – 2700 K) in shock-heated H$_2$-O$_2$-CO-CO$_2$-Ar mixtures. A study in 1986 was conducted by Malerich and Scanlon [51] in which measurements from a homogeneous reactor were compared to theoretical calculations of the radiative recombination of CO and O.

Only a few studies in the 1990’s were conducted concerning CO$_2^*$ chemiluminescence. One of the more significant was from Samaniego et al. [4] in 1995, in which it was determined that CO$_2^*$ accounts for more than 95% of chemiluminescence in CH$_4$-O$_2$-N$_2$ flames over the spectral interval of 340 to 600 nm. In this study, it was determined that CO$_2^*$ chemiluminescence correlated with various flame characteristics, such as fuel consumption rate, heat release rate, and H-atom concentration.

In 2002, Kim et al. [2] made detailed spectral measurements in SI, HCCI, and SCCI engines from various excited state species and determined that CO$_2^*$ emission
correlated well with heat release. Bessler et al. [34] conducted a study in 2003 concerning carbon dioxide laser-induced fluorescence (LIF) in high-pressure methane flames, in which the broad continuum (200 to 450 nm) was attributed to CO$_2^*$. Shortly thereafter, in 2004, Lee et al. [37] conducted UV planar laser-induced fluorescence (PLIF) measurements of CO$_2^*$ in laminar methane-air flames at pressures up to 20 atm. They found that CO$_2$ detection is highly temperature dependent and could potentially be used to infer temperature in practical combustion devices.

In the last five years, several works regarding CO$_2^*$ chemiluminescence have been noteworthy. In 2007 and 2008, Nori and Seitzman [5, 8] made OH*, CH*, and CO$_2^*$ chemiluminescence measurements in syngas and methane flames and observed good agreement with model predictions. CO$_2^*$ measurements were made by Schuermans et al. [46] in 2010 in thermo-acoustic modeling of a gas turbine, and in 2011, Gupta et al. [1] studied the use of CO$_2^*$ chemiluminescence in natural gas-fired reciprocating engines, attributing over 90% of the integrated emission signal over the visible spectrum to CO$_2^*$. They also pointed out that the CO$_2^*$ mechanism is in need of refinement, thus facilitating the need for the current study.

In a 2011 work, Vesel et al. [41] studied dissociation of CO$_2$ molecules in a microwave plasma at high temperatures (up to 2500 K) and observed a high continuum, attributing it to CO$_2^*$ chemiluminescence. Kopp et al. [72] formulated a first-generation kinetics mechanism for CO$_2^*$ chemiluminescence in 2012 and compared model predictions to shock-tube experimental data at low and elevated pressures. This recent work by the present author brought about the need for further chemical kinetics
refinement. A number of other recent works concerning CO$_2$* were conducted recently [45, 64-67, 69], but these concern measurements in the infrared (IR) range, which is associated with vibrational rather than electronic transitions.

**Kinetics Theory**

*CO$_2$* Reaction Kinetics

Although a number of works have addressed possible mechanisms for the formation and depletion of CO$_2$* [4, 8, 35, 36, 40, 42, 48-59], there is no complete consensus as to the full reaction set. One of the most fundamental theories governing CO$_2$* formation is the proportional relationship between CO$_2$* emission intensity and the concentration product of atomic oxygen and carbon dioxide, shown by Equation 1 [35, 36, 38, 43, 47, 48, 52, 57, 58, 62, 63, 68, 73].

$$CO_2^* \propto [CO][O]$$

(1)

This relationship has been shown to fairly accurately predict peak-magnitude temperature dependence at low and elevated pressures, as seen in the work of Kopp et al [72], but it still does not provide a reaction rate that can be incorporated into chemical kinetics mechanisms, which is of the form

$$k = AT^n \exp \left( \frac{-E_a}{\bar{R}T} \right)$$

(2)

where $k$ is the rate coefficient, $A$ is the pre-exponential factor, $n$ is the temperature exponent, $E_a$ is the activation energy, and $\bar{R}$ is the universal gas constant.
The main reaction that goes to forming CO$_2^*$ has been shown by Laidler and Schuler [59] and Broida and Gaydon [60] to be R1, although its rate has not been directly measured. It is the goal of this study to provide a rate for this reaction that accurately predicts measured CO$_2^*$ trends. However, to use experimental data to systematically tailor this rate, the supporting CO$_2^*$ chemistry must be determined. A first-generation mechanism for CO$_2^*$ was recently established by Kopp et al. [72], the formulation of which is briefly described here.

First, thermodynamic calculations were made to determine the reactions that were energetic enough to produce CO$_2^*$. This step was done by calculating the heat of reaction, $H_R$, for every reaction in the ground-state chemical kinetics mechanism that contained CO$_2$ as a participant. The heat of reaction was calculated using Equation 3:

$$H_R = \sum_i N_i \left( \tilde{h}^0_{i,j} \right)_{products} - \sum_j N_j \left( \tilde{h}^0_{j,i} \right)_{reactants}$$  \hspace{1cm} (3)

where $N$ is the number of moles, $\tilde{h}^0$ is the heat of formation at the reference state (298 K, 1 atm), and the subscripts $i$ and $j$ denote each product and reactant species, respectively.

Next, the energy difference, $\Delta E$, between the ground-state (CO$_2$) and the excited state (CO$_2^*$), was calculated using Equation 4,

$$\Delta E = \frac{hc}{\lambda} N_A$$  \hspace{1cm} (4)

where $h$ is Planck’s constant ($6.626\times10^{-34}$ J-s), $c$ is the speed of light ($3\times10^8$ m/s), $\lambda$ is the wavelength of the chemiluminescence transition, and $N_A$ is Avogadro’s Number ($6.022\times10^{23}$ mole$^{-1}$). An average value of 495 nm was used for the wavelength of CO$_2^*$.
chemiluminescence transition, assuming CO$_2^*$ is present at wavelengths between 340 and 650 nm. The reactions in which $H_R$ was greater than $\Delta E$ were then identified as being energetic enough to produce CO$_2^*$. These are denoted by R1 and R2 in Table 1.

**Table 1.** Reaction mechanism for CO$_2^*$. Units are cal, cm, mole, sec, K.

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>$A$</th>
<th>$n$</th>
<th>$E_a$</th>
<th>Source</th>
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<tr>
<td>R1</td>
<td>CO + O + M $\rightleftharpoons$ CO$_2^*$ + M</td>
<td>4.00x10$^{14}$</td>
<td>0</td>
<td>2384</td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td>Efficiency Factors: H$_2$ 2, H$_2$O 12, CO 1.75, CO$_2$ 3.6, Ar 0.7, He 0.7</td>
<td></td>
<td></td>
<td></td>
<td>NUIG Ground-state</td>
</tr>
<tr>
<td>R2</td>
<td>HCO + O $\rightleftharpoons$ CO$_2^*$ + H</td>
<td>3.00x10$^{13}$</td>
<td>0</td>
<td>0</td>
<td>NUIG Ground-state</td>
</tr>
<tr>
<td>R3</td>
<td>CO$_2^*$ + Ar $\rightleftharpoons$ CO$_2$ + Ar</td>
<td>8.42x10$^{12}$</td>
<td>0.5</td>
<td>0</td>
<td>This Work</td>
</tr>
<tr>
<td>R4</td>
<td>CO$_2^*$ + H$_2$O $\rightleftharpoons$ CO$_2$ + H$_2$O</td>
<td>8.34x10$^{12}$</td>
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<tr>
<td>R5</td>
<td>CO$_2^*$ + CO$_2$ $\rightleftharpoons$ CO$_2$ + CO$_2$</td>
<td>9.12x10$^{12}$</td>
<td>0.5</td>
<td>0</td>
<td>This Work</td>
</tr>
<tr>
<td>R6</td>
<td>CO$_2^*$ + CO $\rightleftharpoons$ CO$_2$ + CO</td>
<td>9.69x10$^{12}$</td>
<td>0.5</td>
<td>0</td>
<td>This Work</td>
</tr>
<tr>
<td>R7</td>
<td>CO$_2^*$ + H $\rightleftharpoons$ CO$_2$ + H</td>
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<tr>
<td>R8</td>
<td>CO$_2^*$ + H$_2$ $\rightleftharpoons$ CO$_2$ + H$_2$</td>
<td>2.27x10$^{13}$</td>
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<tr>
<td>R9</td>
<td>CO$_2^*$ + O$_2$ $\rightleftharpoons$ CO$_2$ + O$_2$</td>
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<tr>
<td>R10</td>
<td>CO$_2^*$ + O $\rightleftharpoons$ CO$_2$ + O</td>
<td>9.82x10$^{12}$</td>
<td>0.5</td>
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<tr>
<td>R11</td>
<td>CO$_2^*$ + OH $\rightleftharpoons$ CO$_2$ + OH</td>
<td>9.87x10$^{12}$</td>
<td>0.5</td>
<td>0</td>
<td>This Work</td>
</tr>
<tr>
<td>R12</td>
<td>CO$_2^*$ + CH$_4$ $\rightleftharpoons$ CO$_2$ + CH$_4$</td>
<td>1.19x10$^{13}$</td>
<td>0.5</td>
<td>0</td>
<td>This Work</td>
</tr>
<tr>
<td>R13</td>
<td>CO$_2^*$ + N$_2$ $\rightleftharpoons$ CO$_2$ + N$_2$</td>
<td>9.96x10$^{12}$</td>
<td>0.5</td>
<td>0</td>
<td>This Work</td>
</tr>
<tr>
<td>R14</td>
<td>CO$_2^*$ $\rightleftharpoons$ CO$_2$ + hv</td>
<td>1.00x10$^{0}$</td>
<td>0</td>
<td>0</td>
<td>This Work</td>
</tr>
</tbody>
</table>

The next step was to formulate Arrhenius rate coefficients ($A, n,$ and $E_a$) to use for these reactions in the chemical kinetics mechanism, as shown in Equation 2. These were taken to be the same as their respective ground-state reactions. In addition to R1 and R2, CO$_2^*$ consumption reactions were added, denoted by R3 – R13 in Table 1,
which included quenching from 11 common quenching partners. The rate coefficients for these reactions were calculated based on the hard-sphere collision theory, as discussed in the following section. The last reaction in the mechanism, R14, is the spontaneous emission reaction, and its rate was estimated to be $1 \times 10^6$ sec$^{-1}$. Since a direct measurement of this rate could not be found, it was taken to be similar to those that have been measured for NO* ($4.55 \times 10^6$ sec$^{-1}$), OH* ($1.45 \times 10^6$ sec$^{-1}$), and CH* ($1.85 \times 10^6$ sec$^{-1}$) [21], which all agree with Gaydon’s observation that radiative lifetimes for transitions in the visible and ultra-violet range from $10^{-8}$ to $10^{-6}$ sec [42].

Finally, new thermodynamic data for CO$_2$* were developed. These data are most commonly in the form of the three following polynomial fits:

$$
\frac{c_p^0}{k} = a_{1k} + a_{2k}T_k + a_{3k}T_k^2 + a_{4k}T_k^3 + a_{5k}T_k^4
$$

(5)

$$
\frac{H^0}{RT_k} = a_{1k} + \frac{a_{2k}}{2}T_k + \frac{a_{3k}}{3}T_k^2 + \frac{a_{4k}}{4}T_k^3 + \frac{a_{5k}}{5}T_k^4 + \frac{a_{6k}}{T_k}
$$

(6)

$$
\frac{S^0}{R} = a_{1k} \ln(T_k) + a_{2k}T_k + \frac{a_{3k}}{2}T_k^2 + \frac{a_{4k}}{3}T_k^3 + \frac{a_{5k}}{4}T_k^4 + a_{7k}
$$

(7)

where the seven coefficients, $a_{1-7}$, for each species, $k$, are used to characterize the three thermodynamic properties of that species: $c_p$ (constant pressure specific heat), $H^0$ (enthalpy), and $S^0$ (entropy). Since these coefficients are specified for two temperature ranges, 300 – 1000 K and 1000 – 5000 K, there are a total of 14 thermodynamic coefficients for each species.

To simplify calculations, it was assumed that $c_p$ and $S^0$ for CO$_2$* were the same as the ground state values. A similar assumption is typically made for the other, more well known chemiluminescent species OH* and CH*. This assumption left $a_6$ as the
only unknown coefficient for both temperature ranges. This coefficient was determined by first calculating the enthalpy of formation of CO$_2^*$ ($\Delta H_{f,CO_2^*}$) by adding $\Delta E$ to the enthalpy of ground state CO$_2$. Then for each of the two temperature ranges, $a_6$ was calculated by iteratively changing the coefficient in Equation 6 until $H^o / \bar{R}T$ matched $\Delta H_{f,CO_2^*} / \bar{R}T$. A temperature of 300 K was used for the low-temperature range calculations, and 1000 K was used for the high-temperature range calculations. The resulting thermodynamic data can be found in the Appendix, where $a_6$ was calculated as $-3.74 \times 10^2$ for the low-temperature range and $-1.03 \times 10^3$ for the high-temperature range.

**Quenching Theory**

Quenching is the process in which an electronically excited species is returned to its ground state due to a collision with another molecule [59, 74], represented by the general expression,

$$A^* + B \rightarrow A + B$$

(8)

where $A$ is the molecule being quenched, and $B$ is the colliding molecule. For a bimolecular reaction such as this, the rate coefficient is given by

$$k = Z e^{-E_a / \bar{R}T}$$

(9)

where $Z$ is the frequency of collisions per volume per unit concentration. From basic collision theory, the collision frequency is given by

$$Z = \sigma_{AB}^2 \left[ \frac{8\pi k_B T}{\mu_{AB}} \right]^{1/2}$$

(10)
where $\sigma_{AB}$ is the mean collision diameter of molecules A and B, $k_b$ is the Boltzmann constant (1.381×10^{-23} \text{ J K}^{-1})$, and $\mu_{AB}$ is the reduced mass of the collision pair [59].

A basic interpretation of the proposed theory is to assume $E_a = 0$, in which case the rate coefficient is equal to the collision frequency, and the remaining terms in Equation 2 reduce to $n = \frac{1}{2}$ and

$$A = N_A \sigma_{AB}^2 \left[ \frac{8\pi k_b}{\mu_{AB}} \right]^{1/2} \quad \text{(11)}$$

In this way, the rate expressions for the quenching reactions for CO$_2^*$ were determined for 11 common collision partners, denoted by R3 – R13 in Table 1. The molecular parameters necessary for these calculations are listed in Table 2.

**Table 2.** Molecular parameters used in the hard-sphere calculations for CO$_2^*$ quenching reactions, taken from Turns [75].

<table>
<thead>
<tr>
<th>Species</th>
<th>Collision Diameter (m)</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>3.941×10^{-10}</td>
<td>44.01</td>
</tr>
<tr>
<td>Ar</td>
<td>3.542×10^{-10}</td>
<td>39.948</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>2.641×10^{-10}</td>
<td>18.016</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.941×10^{-10}</td>
<td>44.011</td>
</tr>
<tr>
<td>CO</td>
<td>3.690×10^{-10}</td>
<td>28.01</td>
</tr>
<tr>
<td>H$_2$</td>
<td>2.827×10^{-10}</td>
<td>2.016</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3.467×10^{-10}</td>
<td>31.999</td>
</tr>
<tr>
<td>OH</td>
<td>3.147×10^{-10}</td>
<td>17.007</td>
</tr>
<tr>
<td>H</td>
<td>2.708×10^{-10}</td>
<td>1.008</td>
</tr>
<tr>
<td>O</td>
<td>3.050×10^{-10}</td>
<td>16</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3.758×10^{-10}</td>
<td>16.043</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.798×10^{-10}</td>
<td>28.013</td>
</tr>
</tbody>
</table>
CHAPTER III
EXPERIMENTAL SETUP AND MODELING

Shock-Tube Experimental Setup

Experiments were performed in the high-pressure, stainless-steel shock-tube facility described in detail by Aul [76]. It consists of a 4.93-m long driver section and a 4.72-m driven section, separated by a polycarbonate or aluminum diaphragm. When the driver section is pressurized by an inert gas (helium, in this case), the diaphragm bursts, sending a shock wave to propagate through the driven section of the tube, which is filled to a lower pressure with the gas mixture of interest before the start of each test. The reflection of this shock wave off the endwall of the shock tube creates the high-temperature and -pressure conditions necessary for these measurements.

The temperature and pressure behind the reflected shock wave were determined using standard 1-D shock relations. At five intervals along the driven section of the shock tube, PCB-P113A pressure transducers mounted flush with the inner surface of the tube signal the passage of the shock wave, which determines the incident-shock velocity recorded by four Fluke PM 6666 time-interval counters. The final shock velocity is then extrapolated to the endwall location. The uncertainty in temperature using this method is less than 10 K [77].

The mixtures in this study were manometrically prepared in a stainless steel mixing tank with a perforated stinger along the center of the tank to facilitate rapid,
turbulent mixing. High-purity gases (H₂, Ar – 99.999%, CO – 99.9%, N₂O – 99.5%) were used to prepare the test mixtures. Dilution levels were maintained at 95.95% Ar to minimize subsequent heat release and pressure rise due to the combustion process, so that temperature and pressure would remain constant at the test conditions to allow for more-accurate chemical kinetics modeling. Details on the mixtures used in this study are provided in a later section.

Chemiluminescence light emission was collected through a Sapphire window 1.6 cm from the endwall at a sidewall location. The light from the window passed through a 1-mm slit and focused onto a Hamamatsu 1P21 photomultiplier tube (PMT) after passing through an optical filter housed just outside in a custom-made enclosure. To capture CO₂* chemiluminescence, an optical filter centered at 415 nm was used, which lies within the broadband spectrum of CO₂*, as shown in Figure 1. In a study by Kopp et al. [72], it was confirmed that at these experimental conditions, the emission through either a 458-nm or a 415-nm filter gave the same results, so the 415-nm filter was chosen for this study, which gave better signal-to-noise ratios than the 458-nm filter.

**Chemical Kinetics Modeling**

All kinetics calculations were performed using the homogeneous batch reactor routine in the Chemkin software collection [78], assuming constant volume and constant internal energy. The H₂-O₂ chemistry from the National University of Ireland, Galway (NUIG) formed the baseline mechanism [79, 80], which was fortified by NOₓ chemistry
from the work of Mathieu et al. [81]. The full mechanism, including the CO$_2^*$ chemistry, can be found in the Appendix.

**Experimental Conditions**

The experimental conditions for this study were chosen so that CO$_2^*$ chemiluminescence could be isolated from other emitting species and so that the rate for R1 could be as isolated as possible. Two mixtures were chosen for these purposes, the first of which was taken from the work of Dean et al. [82] who used shock-heated mixtures of H$_2$-N$_2$O-CO-Ar to measure the rate constant of the reaction H + N$_2$O ⇌ N$_2$ + OH*. This mixture was chosen because it exhibited unique characteristics in the various predicted excited-state species time histories, as shown in Figure 2. As seen in Figure 2, the peak concentrations of OH*, CO$_2^*$, and CH$_2$O* occur at noticeably different times, and the shape of the profiles are clearly discernible from one another, making this mixture an ideal one to isolate a particular species, such as CO$_2^*$. 
Figure 2. Model predictions for various chemiluminescence species in $0.0005\text{H}_2 + 0.01\text{N}_2\text{O} + 0.03\text{CO} + 0.9595\text{Ar}$ at 1936 K and 1.5 atm. Profiles are normalized to peak values.

Another compelling reason to choose this mixture was that the predicted peak magnitudes of the other excited-state hydrocarbon species, CH$_2$O* and CH*, were around 6 and 10 orders of magnitude less than the peak magnitude of CO$_2$*, which added confidence that the measured emission from the experiment was primarily from CO$_2$*, as the emission from the other hydrocarbon species would be too low to detect. All measurements in this mixture, denoted as “Mix 0”, were made previously and are presented in the work of Kopp et al. [72].

The second mixture, denoted as “Mix 1”, was a derivative of the first one and chosen to facilitate the determination for R1 in the CO$_2$* reaction mechanism. The mole
fractions of the two mixtures are presented in Table 3, and average experimental conditions are presented in Table 4.

**Table 3.** Mixture compositions for Mix 0 and Mix 1, in % volume.

<table>
<thead>
<tr>
<th></th>
<th>% H₂</th>
<th>% N₂O</th>
<th>% CO</th>
<th>% Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix 0</td>
<td>0.0005</td>
<td>0.01</td>
<td>0.03</td>
<td>0.9595</td>
</tr>
<tr>
<td>Mix 1</td>
<td>0.0005</td>
<td>0.02</td>
<td>0.02</td>
<td>0.9595</td>
</tr>
</tbody>
</table>

**Table 4.** Experimental conditions for Mix 0 and Mix 1 in terms of average pressures and temperature range.

<table>
<thead>
<tr>
<th></th>
<th>Average Pressures (atm)</th>
<th>Temperature Range (K)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix 0</td>
<td>1.4, 10.4</td>
<td>1654 - 2202</td>
<td>Kopp et al. (2012)</td>
</tr>
<tr>
<td>Mix 1</td>
<td>1.5</td>
<td>1700 - 2222</td>
<td>This Work</td>
</tr>
</tbody>
</table>

**Fitting Scheme**

The rate for R1 was determined by an iterative process to match the trends exhibited by the experimental data. The main criterion for the fitting was the CO₂* peak magnitude, which was determined from the PMT measurement for each experiment. A typical time history from the PMT measurement is shown in Figure 3, which shows the rise and fall of CO₂* chemiluminescence for an experiment at 1700 K and 1.6 atm in Mix 1.
Figure 3. Experimental CO$_2^*$ time history showing PMT output in mV as a function of time in microseconds at 1700 K and 1.6 atm in Mix 1.

For each experiment, the CO$_2^*$ time history was recorded, and the peak was graphically determined. In most cases, there was a noticeable double feature in the time history, as seen in Figure 3, with a small hump at the beginning, giving rise to the larger peak later on. For the most part, the second hump was higher than the first, so the peak was always taken to be the maximum from the second feature. This assignment was done to provide consistency in data interpretation, even if the first peak was comparable in magnitude to the second. Note that the experimental time histories presented here were graphically smoothed for presentation purposes. The signal-to-noise ratio was usually between 20 and 70.
To compare experimental trends with model predictions, the peaks were normalized to a common value within that experimental set, which was usually the highest-temperature case. This normalization was done because the PMT measurement is not an absolute concentration measurement of the CO$_2^*$ species, and there was no calibration available that related PMT output in volts to species concentration. Figure 4 shows a plot of the normalized peaks for experiments in Mix 0. Despite the moderate signal-to-noise ratio in the time histories, the resulting scatter in the data in Figure 4 is small.

![Figure 4](image_url)

**Figure 4.** Peak CO$_2^*$ normalized to 2202 K for experiments in Mix 0 at an average pressure of 1.4 atm.
As Figure 4 shows, there is a clear temperature dependence of the peak CO$_2^*$ magnitude, and this trend was a crucial aspect in determining the rate of R1. For each mixture, the peak magnitude trends of the mechanism were compared with the experimental results. As a starting point, the rate for R1 was taken to be the low-pressure rate from the ground-state reaction,

$$CO + O + M \rightleftharpoons CO_2 + M$$

which is a third-order rate and has units of cm$^6$/mole$^2$-sec. In addition, the ground-state collision frequencies were included (see Table 1), and these were not changed throughout the rate determining process. Figure 5 shows an example of the mechanism predictions using this ground-state rate for R1 (i.e., the original, baseline model).

![Peak CO$_2^*$ mechanism predictions with experimental data from Mix 0 using the ground-state rate for R1.](image)

**Figure 5.** Peak CO$_2^*$ mechanism predictions with experimental data from Mix 0 using the ground-state rate for R1.
As Figure 5 shows, the temperature dependence of the CO$_2^*$ peak magnitude is highly under-predicted by this baseline mechanism, as was the case for Mix 1 experiments, and to improve these predictions, sensitivity and rate of production analyses were conducted, which indicated which reactions were most sensitive to the formation and depletion of CO$_2^*$. Typical results of these calculations are shown in Figure 6 at an intermediate temperature for Mix 0 and Mix 1.

Figure 6. CO$_2^*$ sensitivity and rate of production analysis at 1936 K and 1.5 atm for Mix 0 (a), (c) and Mix 1 (b), (d).
Figure 6. Continued.
Figure 6. Continued
The trends are quite similar for both mixtures in terms of which reactions are most sensitive to CO$_2^*$ production and depletion. All results were normalized to a common peak value to allow for direct comparison between the various reactions.

The most important reactions indicated by Figure 6 are as follows:

\[ \text{CO} + \text{O} + \text{M} \rightleftharpoons \text{CO}_2^* + \text{M} \quad \text{R1} \]

\[ \text{CO}_2^* + \text{Ar} \rightleftharpoons \text{CO}_2 + \text{Ar} \quad \text{R3} \]

\[ \text{N}_2\text{O}(+\text{M}) \rightleftharpoons \text{N}_2 + \text{O}(+\text{M}) \quad \text{R15} \]

\[ \text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H} \quad \text{R16} \]
At the time of peak CO$_2^*$, R1 is most sensitive for CO$_2^*$ production, while the argon quenching reaction (R3) is almost equally important for removing CO$_2^*$, seen in Figure 6 (a) and (b). A couple of ground-state reactions also stood out as being sensitive for CO$_2^*$ production and depletion, even though they don’t have CO$_2^*$ as either a product or reactant. The pressure-dependent decomposition reaction of N$_2$O is quite sensitive for CO$_2^*$ production, while reaction R16 is sensitive for CO$_2^*$ destruction. The rate of production analyses shown in Figure 6 (c) and (d) indicate the reactions that go to forming and depleting CO$_2^*$ at these conditions, which are R1 and R3, respectively.

Unfortunately, it was impossible to completely isolate R1 to be the only reaction sensitive to the peak CO$_2^*$. Therefore, the rate of R1 determined in this work was inherently linked to the accuracy of R3, R15, and R16 as well, and uncertainty in R1 due to differences in these rates is presented in Chapter IV.

Since the baseline mechanism under-predicted the peak CO$_2^*$ trends, an increase in the rate for R1 was necessary. It was assumed that the current activation energy (2,384 cal/mole) of this reaction was sufficient, which came from the ground-state reaction chemistry. Changing this parameter to fit the peak trends of the experiments greatly reduced the agreement with species time histories. This fixing of the activation energy left the pre-exponential factor, A, as the variable to be determined in this work. This parameter was incrementally increased until the peak trends from the experiments in Mix 0 and Mix 1 were most accurately predicted in both cases. In addition to peak magnitude agreement, time history agreement was also monitored. Based on peak
magnitude and time history agreement, the pre-exponential factor for R1 was determined as $4.0 \times 10^{14} \text{ cm}^6/\text{mole}^2\text{-sec}$. The full Arrhenius rate expression is as follows:

$$k_{R1} = 4.0 \times 10^{14} \exp (-2,384/\bar{RT}) \text{ cm}^6/\text{mole}^2\text{sec}$$

where the activation energy has units of cal/mole. Final comparisons with this rate to experimental data are presented in the following chapter.
CHAPTER IV

RESULTS AND DISCUSSION

Temperature Dependence of Peak Magnitude

Table 5 lists the CO$_2$* peak magnitude determined from each experiment for Mix 0 and Mix 1 that were used to calculate R1.

Table 5. Temperature, pressure, and peak CO$_2$* signal from the experiments used to determine R1.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (atm)</th>
<th>CO$_2$* Signal Peak (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1712</td>
<td>1.49</td>
<td>49.8</td>
</tr>
<tr>
<td>1761</td>
<td>1.47</td>
<td>59.1</td>
</tr>
<tr>
<td>1818</td>
<td>1.44</td>
<td>64.1</td>
</tr>
<tr>
<td>1936</td>
<td>1.46</td>
<td>84.4</td>
</tr>
<tr>
<td>2006</td>
<td>1.41</td>
<td>101.7</td>
</tr>
<tr>
<td>2105</td>
<td>1.38</td>
<td>119.1</td>
</tr>
<tr>
<td>2202</td>
<td>1.33</td>
<td>136.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (atm)</th>
<th>CO$_2$* Signal Peak (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700</td>
<td>1.56</td>
<td>38.2</td>
</tr>
<tr>
<td>1730</td>
<td>1.55</td>
<td>38.5</td>
</tr>
<tr>
<td>1802</td>
<td>1.54</td>
<td>48.8</td>
</tr>
<tr>
<td>1897</td>
<td>1.48</td>
<td>60.5</td>
</tr>
<tr>
<td>1911</td>
<td>1.56</td>
<td>64.6</td>
</tr>
<tr>
<td>1927</td>
<td>1.47</td>
<td>63.0</td>
</tr>
<tr>
<td>2015</td>
<td>1.44</td>
<td>75.4</td>
</tr>
<tr>
<td>2108</td>
<td>1.41</td>
<td>86.5</td>
</tr>
<tr>
<td>2205</td>
<td>1.42</td>
<td>104.5</td>
</tr>
<tr>
<td>2222</td>
<td>1.38</td>
<td>101.7</td>
</tr>
</tbody>
</table>
The data are presented graphically in Figure 7 along with the mechanism predictions using the final rate determined for R1, which was $4.0 \times 10^{14} \exp(-2.384/RT)$ cm$^6$/mole$^2$-sec as mentioned above and summarized in Table 1.

![Figure 7](image-url)

**Figure 7.** Normalized peak CO$_2^*$ from experiments compared with final mechanism predictions for Mix 0 (a) and Mix 1 (b).

Using this rate for R1 along with the supporting chemistry described in Chapter III, Figure 7 shows that the model very accurately predicts the CO$_2^*$ peak magnitude temperature dependence trends in both mixtures. It is shown in a later section that the model also does well at predicting peak CO$_2^*$ trends at higher pressures and does a fairly good job at predicting trends in a methane-based mixture.
Species Time Histories

Aside from peak magnitude trends, it was also important to consider overall CO$_2$* species time histories in determining the rate for R1. Figure 8 shows the final mechanism predictions in comparison with experiments in Mix 0 and Mix 1. Three temperatures are presented to show the evolution of the species time history as temperature is increased. The profiles were normalized to peak values to allow for comparison between model and data. In addition, the profiles predicted by the mechanism were shifted in time to align with the initial rise of CO$_2$* from the experiment to facilitate comparison of the overall shape of the profiles.

**Figure 8.** Normalized CO$_2$* experimental profiles compared with the final mechanism predictions for low, medium, and high temperature in Mix 0 (a), (c), (e) and Mix 1 (b), (d), (f).
The CO$_2^*$ experimental profiles in both mixtures exhibited a double feature, with a small, sometimes very subtle incipient hump giving rise to a larger and broader maximum in the profile. The two features are slightly more discernible in Mix 1, with the first hump closer in magnitude to the second. This is a rather unique feature, and the fact that the mechanism picks up on it is quite promising. While the agreement is not
perfect, the small subtleties in the experimental time histories are present in the mechanism predictions, and perhaps agreement could be improved with slight adjustments in the ground-state chemistry.

In Mix 0, the leading edge of the CO$_2^*$ experimental profile is fairly accurately modeled by the mechanism at all three temperatures, as seen in Figure 8 (a), (c), and (e). However, the trailing edge is slightly under-predicted by the mechanism, which predicts a faster CO$_2^*$ decay than the experiment at these conditions. The trailing edge is better predicted by the mechanism in Mix 1, as seen in Figure 8 (b), (d), and (f), although the incipient rise is slightly under-predicted at the low (b) and moderate (d) temperatures. In most cases, for both mixtures, the mechanism predicts a faster peak than the experiment, but not by much. Changes to the CO$_2^*$ chemistry will most likely not change this answer, as the excited-state chemistry mostly governs the peak magnitudes of a species and not the overall shape. The timing of the species is more dependent rather on the ground-state chemistry, which in this case R15 and R16 could have an effect on this parameter, as shown by the sensitivity analyses in Figure 6 (a) and (b).

**Uncertainty**

Since it was not possible to completely isolate R1 to determine its rate, it was necessary to consider upper and lower bounds on a few of the other reactions that were sensitive in the formation and depletion of CO$_2^*$. The reactions considered in this
uncertainty analysis were R3, R15, and R16, as these were shown in Figure 6 (a) and (b) to be most sensitive for CO$_2^*$ formation and consumption.

Figure 9 shows the effect of an increase and decrease of one order of magnitude in the pre-exponential factor of R3, the CO$_2^*$ quenching rate by argon.

![Graph](attachment:image_url)

**Figure 9.** Effect of changes to $CO_2^* + Ar \rightleftharpoons CO_2 + Ar$ (R3) on mechanism predictions compared to normalized CO$_2^*$ peak trends from experiments in Mix 0 (a) and Mix 1 (b).

As expected, an order of magnitude increase in this rate causes an under-prediction of the peak magnitude trend by about 20% in both mixtures. This result is due to the negative sensitivity of this reaction to the formation of CO$_2^*$, so an increase in this rate would decrease the amount of CO$_2^*$ produced. Conversely, an order of magnitude decrease in this rate causes an over-prediction of peak magnitude trends by about 30% in Mix 0 and 25% in Mix 1. It should be noted that this rate has never been measured or validated, and its current value is based on the hard sphere theoretical calculations.
presented in Chapter II. In OH* chemistry, a species that has been studied more extensively, quenching by argon has been measured to be up to two orders of magnitude less than theoretical calculations [15, 19]. However, in a study by Holtermann et al. [83], measured quenching by argon of SO$_2$* was comparable to theoretical calculations, as was quenching by argon of propynal in a study by Thayer and Yardley [84]. Therefore, it was concluded that an order-of-magnitude increase or decrease in this rate (R3) would be sufficient in determining the uncertainty limits in calculations for R1.

The next most important rate in CO$_2$* formation was R15, which came from the NO$_x$ ground-state chemistry submechanism. Figure 10 shows the effect of an increase in this rate by about five times and a decrease by about 15 times. These upper and lower bounds came from the general consensus of variation in the rate from both theoretical and experimental studies [85]. There is little effect of increasing this rate to its upper limit, as shown by the dotted line in Figure 10. However, decreasing this rate by about 15 times leads to an under-prediction of peak CO$_2$* by around 20% in Mix 0 and 30% in Mix 1. The higher-percentage difference in Mix 1 is most likely due to the increase of N$_2$O present in this mixture compared to Mix 0.
**Figure 10.** Effect of changes to $N_2O(+M) \rightarrow N_2 + O(+M)$ (R15) on mechanism predictions compared to normalized CO$_2^*$ peak trends from experiments in Mix 0 (a) and Mix 1 (b).

The last reaction considered in the uncertainty analysis was R16, which displays a negative sensitivity to CO$_2^*$ at the time of peak CO$_2^*$ formation, as shown by Figure 6 (a) and (b) in Chapter III. The effect of increasing this rate by around three times and decreasing it by around six times is shown in Figure 11. Again, these upper and lower bounds were based on the general variation in this rate from a mass of past theoretical and experimental studies [85].
The upper limit of this rate causes around a 20% under-prediction of peak CO$_2$* trends in both mixtures, while the lower limit leads to an over-prediction of peak CO$_2$* by about 25% in Mix 0 and 15% in Mix 1.

Two other minor parameters were also considered in the uncertainty: the effect of the efficiency factors used for R1 and the effect of R2, the CO$_2$* formation reaction $HCO + O \rightleftharpoons CO_2^* + H$ (see Table 1). Since the sensitivity analyses did not identify R2 as an important reaction for CO$_2$*, it was of interest to check whether its inclusion in the mechanism made a difference in the final mechanism predictions. Figure 12 shows the effect of omitting the efficiency factors used for R1 and the effect of omitting R2. As expected, these two parameters have little to no effect on the final mechanism predictions.
Figure 12. Effect of omitting the efficiency factors for $CO + O + M \rightleftharpoons CO_2^* + M$ (R1) and omitting $HCO + O \rightleftharpoons CO_2^* + H$ (R2) on mechanism predictions compared to normalized CO$_2^*$ peak trends from experiments in Mix 0 (a) and Mix 1 (b).

The effect of a combination of the upper and lower bounds of the three most sensitive rates (R3, R15, and R16) would result in about a 35% under-prediction and around a 40% over-prediction of experimental trends in Mix 0. Combining the uncertainties in Mix 1 leads to about a 43% under-prediction and around a 30% over-prediction of experimental trends. These overall uncertainties were calculated by combining the individual uncertainties for each rate in a sum-of-squares fashion.

Comparisons with Past Works

In a previous study at this research facility, CO$_2^*$ emission was monitored at 337 nm in a stoichiometric methane-oxygen mixture diluted in 99.1% Ar [9]. Figure 13
shows the CO$_2^*$ peak magnitude trends with temperature of that study at an average pressure of 1.3 atm compared with the mechanism predictions of this work. Because this mixture contained CH$_4$, the mechanism was fortified by the NUIG C4_54.1 chemistry, which can be found at http://c3.nuigalway.ie/mechanisms.html.

![Graph showing normalized peak CO$_2^*$]({"normalized_peak_CO2\_star.png"}

**Figure 13.** Normalized peak CO$_2^*$ from experiments by Petersen et al. [9] in a stoichiometric mixture of methane and oxygen highly diluted in argon at an average pressure of 1.3 atm compared with mechanism predictions from this work.

As the figure shows, there is a slight over-prediction of the data by the model. Although the trend is not completely captured by the mechanism using the rate for R1 determined here, the prediction is far better than what was presented in the original work, shown by the dashed line, which led to over a four-fold over-prediction of the data.
A species time history comparison is presented in Figure 14, which compares an experimental CO$_2^*$ profile from [9] to the mechanism predictions from this work at 2092 K and 1.2 atm.

**Figure 14.** Normalized CO$_2^*$ experimental profile at 2092 K and 1.2 atm from [9] compared with the mechanism prediction from this work.

The agreement here is quite good in that the width of the experimental profile is very closely matched with the mechanism prediction. The trailing edge is slightly over-predicted by the mechanism, but this is an extreme improvement over what was presented in the original work, shown by the dashed line, which was around a five-fold over-prediction of the trailing edge. Note that the time history as predicted by the model
was shifted in time to align with the peak of the experimental profile to allow for comparison of the general shape of the profile.

The ability of the mechanism from this work to fairly accurately predict CO$_2^*$ peak trends and species time histories in a hydrocarbon mixture adds confidence to the formulations of R1 made herein. It was also of interest to make comparisons with past literature rates of R1. Although only one study has ever quoted a third-order rate for R1 [40], a work by Slack and Grillo [58] formulated a general relationship between CO$_2^*$ emission intensity, $i_{CO_2^*}$, and the concentration product of [CO] and [O] given by,

$$i_{CO_2^*} = 3.3(\pm0.3) \times 10^3 \exp (-2,300/T)[CO][O]$$

where temperature is in K and concentration units are mole/cm$^3$. Figure 15 and Figure 16 show the experimental results from this study compared with these two rate expressions alongside the mechanism predictions from this work. As Figure 15 shows, both rate expressions from the literature are quite good at modeling the peak CO$_2^*$ trends of the data in both mixtures, although the rate from Sulzmann et al. [40] slightly over-predicts peak trends in Mix 1.
Figure 15. Normalized peak CO$_2$* from experiments compared with mechanism predictions from this work, Slack and Grillo [58], and Sulzmann et al. [40] for Mix 0 (a) and Mix 1 (b).

Species time history comparisons are presented in Figure 16 for a moderate temperature in Mix 0 (a) and Mix 1 (b). Time histories from the model predictions were aligned to the rise in CO$_2$*, rather than the peak, which provided a better visual comparison.
Figure 16. Normalized CO$_2$* experimental profiles compared with mechanism predictions from this work, Slack and Grillo [58], and Sulzmann et al. [40] at 1936 K and 1.5 atm in Mix 0 (a) and 1927 K and 1.5 atm in Mix 1 (b).

In Mix 0 (Figure 16 (a)), the leading edge is most closely modeled by the rate for R1 from this work, compared with the other two rate expressions, while the rate expression from Slack and Grillo is the best at modeling the trailing edge of the CO$_2$* species profile. For Mix 1 (Figure 16 (b)), the trailing edge of the CO$_2$* profile is again most closely modeled by the rate expression from Slack and Grillo, while the rate from Sulzmann et al. is best at modeling the leading edge. In both cases, the rate for R1 developed in this work falls between the two rate expressions from Slack and Grillo and Sulzmann et al.

Figure 17 shows a typical Arrhenius plot of the natural logarithm of the rate constant for R1 developed in this work compared with that from Sulzmann et al. The
rate for R1 developed by Sulzmann et al. was for a temperature range of 1500 to 3000 K and is as follows:

\[ k_{R1} = 2.2 \times 10^{15} \exp \left( -3,700/\bar{RT} \right) \text{cm}^6/\text{mole}^2s \]

where the units for the activation energy are cal/mole. The rate expression from Slack and Grillo could not be included in this plot, as it is only a relation between peak intensity and species concentrations and not a kinetic rate. While the magnitudes of the two rates differ (due to the order of magnitude difference in the pre-exponential factor of both rates), the slopes (indicative of activation energy) are similar, as seen in Figure 17.

**Figure 17.** Termolecular rate constants for R1 from Sulzmann et al. and this work plotted against inverse temperature.
High-Pressure Excursion

In the work of Kopp et al. [72], experiments in Mix 0 were also performed at elevated pressures, and it was of interest to compare those results to the model predictions from this work. Figure 18 shows the normalized peak CO$_2^*$ trends from the experiments compared with the mechanism developed here.

![Figure 18.](image)

**Figure 18.** Normalized peak CO$_2^*$ from experiments in Mix 0 at an average pressure of 10.5 atm compared with mechanism predictions from this work.

Even though the rate for R1 was calculated using low-pressure data, its ability to predict trends at elevated pressures in Mix 0 is excellent. The experimental CO$_2^*$ species time histories are also predicted well by the mechanism, shown in Figure 19. The profiles as
predicted by the model were shifted in time to align with the peak of the experimental profile.

Figure 19. Normalized CO$_2$* experimental profiles compared with final mechanism predictions at 1654 K and 10.6 atm (a) and 2176 K and 10.5 atm (b).

For the low-temperature case in Figure 19 (a), the mechanism does an exceptional job at predicting the shape of the CO$_2$* profile. The agreement between model and experiment slightly lessens as temperature increases, as shown in Figure 19 (b), with the model tending to predict slightly thinner species profiles than the experiment. However, this phenomenon is quite common among high-pressure shock-tube measurements of chemiluminescence species. Overall, the ability of the mechanism to predict high-pressure trends is quite promising.
CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

$\text{CO}_2^*$ chemiluminescence measurements were performed in $\text{H}_2-\text{N}_2\text{O}-\text{CO}-\text{Ar}$ mixtures behind reflected shock waves to evaluate $\text{CO}_2^*$ chemical kinetics. The experimental results were used to tailor the rate of the main $\text{CO}_2^*$ formation reaction, $\text{CO} + \text{O} + \text{M} \rightleftharpoons \text{CO}_2^* + \text{M} \ (R1)$. Supporting $\text{CO}_2^*$ quenching chemistry was determined from basic collision theory. The overall rate expression for $R1$ was determined as

$$k_{R1} = 4.0 \times 10^{14} \exp \left( -2.384/\bar{R}T \right) \text{cm}^6/\text{mole}^2\text{sec}$$

where units of the activation energy are cal/mole. The final mechanism was able to reproduce peak $\text{CO}_2^*$ trends at both low and elevated pressures in the $\text{H}_2-\text{N}_2\text{O}-\text{CO}-\text{Ar}$ mixtures. Comparisons with shock-tube data in methane-oxygen mixtures were also made, which showed a slight over-prediction of peak $\text{CO}_2^*$ experimental trends.

The unique species time histories of $\text{CO}_2^*$ in the $\text{H}_2-\text{N}_2\text{O}-\text{CO}-\text{Ar}$ mixtures offered a good test for the mechanism. Although trends were not perfectly matched, the subtleties in the experimental profiles were captured by the mechanism, and slight refinements in some key ground-state reactions could further improve these predictions. Because the rate for $R1$ could not be completely isolated, its uncertainty was inherently related to the accuracy in a few other reactions, one of which was the quenching of $\text{CO}_2^*$ by argon. Uncertainty analysis showed that variation in this rate by an order of magnitude caused up to a 30% under- or over-prediction of peak $\text{CO}_2^*$ trends. Since this rate was determined purely by theoretical calculations, it is recommended that
experiments to validate this rate should be made to add confidence in the value
determined for R1.

Now that a full kinetic scheme for CO$_2^*$ has been developed, another avenue of
research would be to make quantitative measurements of CO$_2^*$ by performing a series of
low-pressure calibration measurements to correlate PMT output to absolute CO$_2^*$
concentration, much like what was done for OH* in the work of Petersen et al. [9].
Coupled with measurements at elevated pressures, this procedure could provide insight
into a possible pressure dependence of R1.
REFERENCES


[36] Davies, W.O., "Carbon Dioxide Dissociation at 6,000 to 11,000 K," The Journal of Chemical Physics, 43, 8, (1965), pp. 2809-2818.


APPENDIX

Detailed Kinetics Mechanism

ELEMENTS
C H N O AR HE
END
SPECIES
H H2 O O2 OH OH*
H2O N2 HO2 H2O2 AR
CO CO2 HE CH4 C2H6 HCO
N NH NO N2H
NH2 N2O3 HNO NO2 NNH NH3 N2H2
HONO NO3 HNO3 N2H3 N2H4 N2O4 NH2OH
HN OH H2NO HNNO CO2(A)
END
REACTIONS
H+O2<=>O+OH 9.65E+14 -0.262 1.62E+04
O+H2<=>H+OH 5.080E+04 2.670 6.292E+03
OH+H2<=>H+H2O 2.247E8 1.520 3.450E+03
!REF: SUTHERLAND ET AL., 23RD SYMPOSIUM, P. 51 (1990) INCREASED BY 16% FOR H2-CO-H2O FLAMES
OH+H2<=>O+H+M 6.165E+15
!REF: LI, IJCK 36: 566–575, 2004
!REF: OPTIMISED TO FIT H2 AND CH4 FLAMES DATA
H+OH+M<=>H2O+M 6.165E+15 -0.500 0.000E+00
H2/ 2.5/ H2O/ 12/ CO/ 1.9/ CO2/ 3.8/ HE/ .83/ CH4/ 2/ C2H6/ 3/
O+O+M<=>O2+M 6.165E+15 -0.500 0.000E+00
H2/ 2.5/ H2O/ 12/ AR/ .83/ CO/ 1.9/ CO2/ 3.8/ HE/ .83/ CH4/ 2/ C2H6/ 3/
O+H+M<=>OH+M 4.714E+18 -1.000 0.000E+00
H2/ 2.5/ H2O/ 12/ AR/ .75/ CO/ 1.5/ CO2/ 2/ HE/ .75/ CH4/ 2/ C2H6/ 3/
!REF: Li IJCK 36: 566–575, 2004
!REF: OPTIMISED TO FIT H2 AND CH4 FLAMES DATA
H+OH+M<=>H2O+M 6.165E+15 -2.000 0.000E+00
H2/ 2.5/ H2O/ 12/ AR/ 0.38/ HE/ 0.38/ CO/ 1.9/ CO2/ 3.8/ CH4/ 2/ C2H6/ 3/
!REF: FERNANDES PCCP 2008
H+O2(+M)<=>HO2(+M) 4.650E+12 0.440 0.000E+00
LOW/ 1.737E+19 -1.23 0.000E+00/
TROE/ 0.67 1E-30 1E30 1E30/
H2/1.3/ CO/1.9/ CO2/3.8/ HE/0.0/ H2O/10.0/ AR/0.00/ CH4/2/ C2H6/3/
H+O2(+AR)<=>HO2(+AR) 4.650E+12 0.440 0.000E+00
!REF: BATES ET AL. PCCP 3 (2001) 2337-2342
LOW/ 6.810E+18 -1.200 0.0/
TROE/ 0.70 1.0E-30 1.0E+30 1.0E+30/
!REF:LPL * 1.5 AK
H+O2(+HE)<=>HO2(+HE) 4.650E+12 0.440 0.000E+00
LOW/ 9.192E+18 -1.20 0.000E+00/
TROE/ 0.59 1E-30 1E30 1E30/
!REF: MUELLER 99
HO2+H<=>OH+OH 7.079E+13 0.00 2.950E+02
!REF:MICHAEL SUTHERLAND 2000
H2+O2<=>H+HO2 5.176E+05 2.433 5350 2.0
HO2+O<=>OH+O2 3.250E+13 0.000 0.000E+00
!REF:KEYSER, J. PHYS. CHEM. 92:1193 (1988) REDUCED BY 15%
HO2+OH<=>H2O2+O2 2.456E+13 0.000 -4.970E+02
!REF:HIPPLER ET AL. J.CHEM.PHYS 93 1755-1760 (1990)
HO2+HO2<=>H2O2+O2 1.300E+11 0.000 -1630.00
DUP
!REF:REDUCED BY 13%
HO2+HO2<=>H2O2+O2 3.658E+14 0.000 12000.00
DUP
!REF:RATE CONSTANT IS FOR N2
H2O2+H<=>H2+HO2 2.00E+12 0.90 4.8749+04
LOW/ 1.865E+25 -2.30 4.8749+04/
TROE/ 0.51 1E-30 1E+30/
H2O2+M<=>H2+HO2 2.00E+12 0.90 4.8749+04
LOW/ 2.49E+24 -2.30 4.8749+04/
TROE/ 0.43 1E-30 1E+30/
H2O/ 0.0/ CO2/ 1.6/ N2/ 1.5/ O2/ 1.2/ HE/ 0.65/ H2O2/ 7.7/
!REF:EFFICIENCIES FOR H2 AND CO TAKEN FROM LI ET AL., INT. J. CHEM. KINET.
H2/3.7/ CO/2.8/
H2O2+H<=>H2O+OH 2.410E+13 0.000 3.970E+03
H2O2+H<=>H2+HO2 2.150E+10 1.000 6.000E+03
H2O2+OH<=>H2O+HO2 9.550E+06 2.000 3.970E+03
H2O2+OH<=>H2O+HO2 1.74E+12 0.000 3.18E+02
DUP
H2O2+OH<=>H2O+HO2 7.59E+13 0.000 7.269E+03
DUP
!REF:MEULLER 99 * 0.76
CO+O(+M)<=>CO2(+M) 1.362E+10 0.000 2384.00
LOW/ 1.173E+24 -2.79 4191.0/
H2/ 2.0/ H2O/ 12/ CO/ 1.75/ CO2/ 3.6/ AR/ 0.7/ HE/ 0.7/
!REF:86TSA/ HAM * 0.44
CO+O2 <=> CO2+O 1.119E+12 0.000 47700.00
CO+OH <=> CO2+H 7.015E+04 2.053 -355.67
DUP
CO+OH <=> CO2+H 5.757E+12 -0.664 331.83
DUP
!REF:YOU ET AL. J. PHYS. CHEM. A 2007, 111, 4031-4042
CO+HO2 <=> CO2+OH 1.570E+05 2.180 1.794E+04
!REF:LI ET AL. IJCK 2007
HCO+M <=> H+CO+M 4.750E+11 0.660 1.487E+04
H2/ 2/ H2O/ 12/ CO/ 1.5/ CO2/ 2/ CH4/ 2/ C2H6/ 3/
HCO+O2 <=> CO+HO2 7.580E+12 0.000 4.100E+02
HCO+H <=> CO+H2 7.340E+13 0.000 0.000E+00
HCO+OH <=> CO+H2O 1.020E+14 0.000 0.000E+00
!§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§
! NOX REACTIONS §§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§
! NO REACTIONS
N2+O => NO+N 1.80E+14 0.00 76100 ! 41 KONNOV
NO+N = N2+O 2.11E+13 0.00 0 ! 42 BAULCH
N+O2 = NO+O 9.00E+09 1.00 6500 ! 43 KONNOV
NO+M = N+O+M 9.64E+14 0.00 148300 ! 44 KONNOV
N2 /1.5/ NO /3.0/
NO+NO = N2+O2 3.00E+11 0.00 65000 ! 45 KONNOV
NO+O+(M) = NO2+(M) 1.30E+15 -0.75 0 ! 46 KONNOV
LOW /4.72E+24 -2.87 1551/
TROE /0.962 10.0 7962/
AR /0.6/ NO2 /6.2/ NO /1.8/ O2 /0.8/ N2O /4.4/ H2O /10.0/
HO2 + NO = NO2 + OH 2.11E+12 0.00 -479 ! 47 HOWARD, J. AM.
CHEM. SOC., 102, 6937, 1980. (SUGG. BY TSANG)
N+OH = NO+H 2.00E+13 0.00 0 ! 48 MICK AND ROTH, J. PHYS.
CHEM. 98 (1994) 5310-5313.
! NO2 REACTIONS
NO2 + O = NO + O2 3.91E+12 0.00 -238 ! 49 KONNOV
NO2 + N = N2 + O 8.40E+11 0.00 0 ! 50 KONNOV
NO2 + N = NO + NO 1.00E+12 0.00 0 ! 51 KONNOV

62
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**Notes:**
- All reactions are expressed in terms of rate constants and activation energies.
- The temperature for each reaction is specified in Kelvin (K).
- Sources: KONNOV, BAULCH, MEV, DIAU, TROE, H2O/10.0/ O2/0.8/ H2/2.0/.
NO+OH(-M)=HONO(-M) 2.00E+12 -0.05 -721 ! 77 KONNOV
  LOW / 5.08E+23 -2.51 -67.6 /
  TROE/0.62 10.0 100000.0 /
  H2O/10.0/ O2/2.0/ AR/0.75/ H2/2.0/
NO2+H+M=HONO+M 1.40E+18 -1.50 900 ! 78 KONNOV
HONO+H=HNO+OH 5.64E+10 0.86 4970 ! 79 KONNOV
HONO+H=NO+H2O 8.12E+06 1.89 3840 ! 80 KONNOV
HONO+O=OH+NO2 1.20E+13 0.00 5960 ! 81 KONNOV
HONO+OH=H2O+NO2 1.69E+12 0.00 -517 ! 82 KONNOV
HONO+NH=NH2+NO2 1.00E+13 0.00 0 ! 83 KONNOV
HONO+HONO=H2O+NO2+NO 1.00E+13 0.00 8540 ! 84 KONNOV
HONO+NH2=NO2+NH3 5.00E+12 0.00 0 ! 85 KONNOV
+! HNO REACTIONS
HNO+NO=N2O+OH 8.50E+12 0.00 29580 ! 86 KONNOV
HNO+NO+NO=HNNO+NO2 1.60E+11 0.00 2090 ! 87 KONNOV
HNO+H=NO+H2 4.46E+11 0.72 655 ! 89 KONNOV
HNO+OH=NO+H2O 1.50E+24 -3.50 2200 ! 91 KONNOV
HNO+O=OH+NO2 2.00E+12 0.00 2000 ! 92 KONNOV
HNO+O=OH+NO 2.00E+13 0.00 2000 ! 93 KONNOV
HNO+O=NO+H2O 1.00E+11 0.50 2000 ! 94 KONNOV
HNO+OH=H2O+NO 5.00E+10 0.50 3000 ! 95 KONNOV

+! HNO3 REACTIONS
NO2+OH(+M)=HNO3(+M) 2.41E+13 0.00 0 ! 100 KONNOV
HNO+NO2=H2O+NO2 2.00E+13 0.00 0 ! 101 KONNOV
HNO3+H=H2+NO3 5.56E+08 1.53 16400 ! 102 KONNOV
HNO3+H=H2O+NO2 6.08E+01 3.29 6290 ! 103 KONNOV
HNO3+H=OH+HONO 3.82E+05 2.30 6980 ! 104 KONNOV
HNO3+OH=NO3+H2O 1.03E+10 0.00 -1240 ! 105 KONNOV
+! HNNO REACTIONS
NH+NO+M=HNNO+M 1.63E+23 -2.60 1820 ! 106 KONNOV
HNNO+H=H2O+H2 2.00E+13 0.00 0 ! 107 KONNOV
HNNO+H=NH2+NO 1.00E+12 0.00 0 ! 108 KONNOV
HNNO+O=N2O+OH 2.00E+13 0.00 0 ! 109 KONNOV
HNNO+OH=H2O+N2O 2.00E+13 0.00 0 ! 110 KONNOV
HNNO+OH=HNOH+NO 1.00E+12 0.00 0 ! 111 KONNOV
HNNO+NO=N2+HONO 2.60E+11 0.00 1610 ! 112 KONNOV
HNNO+NO=NNH+NO2 3.20E+12 0.00 540 ! 113 KONNOV
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<td>H2O + NO + NO2</td>
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<td>-4.29</td>
<td>60300</td>
<td>!117 KONNOV</td>
</tr>
<tr>
<td>H2NO + M = H2 + NO + M</td>
<td>5.00E+13</td>
<td>0.00</td>
<td>0</td>
<td>!121 KONNOV</td>
</tr>
<tr>
<td>H2NO + O = HNO + OH</td>
<td>3.00E+07</td>
<td>2.00</td>
<td>2000</td>
<td>!122 KONNOV</td>
</tr>
<tr>
<td>H2NO + NO = HNO + HNO</td>
<td>6.00E+11</td>
<td>0.00</td>
<td>2000</td>
<td>!128 KONNOV</td>
</tr>
<tr>
<td>HNOH + M = HNO + H + M</td>
<td>2.00E+24</td>
<td>-2.84</td>
<td>58935</td>
<td>!129 KONNOV</td>
</tr>
<tr>
<td>HNOH + M = HNO + H + M</td>
<td>2.00E+24</td>
<td>-2.84</td>
<td>58935</td>
<td>!129 KONNOV</td>
</tr>
<tr>
<td>HNOH + OH = HNO + H2O</td>
<td>2.40E+06</td>
<td>2.00</td>
<td>-1190</td>
<td>!134 KONNOV</td>
</tr>
<tr>
<td>NH + O = NO + OH</td>
<td>7.60E+10</td>
<td>0.00</td>
<td>1530</td>
<td>!142 MERTENS, CHANG, HANSON, &amp; BOWMAN, IJCK, 23, 173, 1991</td>
</tr>
<tr>
<td>NH + OH = HNO + H</td>
<td>2.00E+13</td>
<td>0.00</td>
<td>0</td>
<td>!143 MERTENS, CHANG, HANSON, &amp; BOWMAN, IJCK, 23, 173, 1991</td>
</tr>
</tbody>
</table>

**H2NO REACTIONS**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Pre-Exp</th>
<th>E-Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2NO + NO = N2O + HNO</td>
<td>1.00E+12</td>
<td>0.00</td>
<td>0</td>
<td>!114 KONNOV</td>
</tr>
<tr>
<td>H2NO + NO2 = N2O + HONO</td>
<td>1.00E+12</td>
<td>0.00</td>
<td>0</td>
<td>!115 KONNOV</td>
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<tr>
<td>H2NO + NO2 = NNH + NO3</td>
<td>1.00E+13</td>
<td>0.00</td>
<td>1700</td>
<td>!116 KONNOV</td>
</tr>
<tr>
<td>H2NO + H = HNO + H2</td>
<td>3.00E+07</td>
<td>2.00</td>
<td>2000</td>
<td>!120 KONNOV</td>
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<tr>
<td>H2NO + H = NH2 + OH</td>
<td>5.00E+13</td>
<td>0.00</td>
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<td>!121 KONNOV</td>
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<tr>
<td>H2NO + O2 = HNO + HO2</td>
<td>6.00E+11</td>
<td>0.00</td>
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<td>!127 KONNOV</td>
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<tr>
<td>H2NO + NO = HNO + HNO</td>
<td>2.00E+07</td>
<td>2.00</td>
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<td>!127 KONNOV</td>
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<tr>
<td>H2NO + NO2 = HONO + HNO</td>
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<td>2.00</td>
<td>13000</td>
<td>!127 KONNOV</td>
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**HNOH REACTIONS**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Pre-Exp</th>
<th>E-Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNOH + M = HNO + H + M</td>
<td>2.00E+24</td>
<td>-2.84</td>
<td>58935</td>
<td>!129 KONNOV</td>
</tr>
<tr>
<td>HNOH + H = HNO + H2</td>
<td>2.40E+06</td>
<td>2.00</td>
<td>-1190</td>
<td>!134 KONNOV</td>
</tr>
<tr>
<td>HNOH + O = HNO + OH</td>
<td>7.00E+13</td>
<td>0.00</td>
<td>0</td>
<td>!132 KONNOV</td>
</tr>
<tr>
<td>HNOH + O2 = HNO + HO2</td>
<td>6.00E+11</td>
<td>0.00</td>
<td>2000</td>
<td>!138 KONNOV</td>
</tr>
<tr>
<td>HNOH + NO = HNO + HO2</td>
<td>1.00E+12</td>
<td>0.00</td>
<td>3000</td>
<td>!139 KONNOV</td>
</tr>
</tbody>
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**NH2OH REACTIONS**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Pre-Exp</th>
<th>E-Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH2OH + OH = HNOH + H2O</td>
<td>2.50E+13</td>
<td>0.00</td>
<td>4250</td>
<td>!140 KONNOV</td>
</tr>
<tr>
<td>NH2OH + OH = HNOH + H2O</td>
<td>2.50E+13</td>
<td>0.00</td>
<td>4250</td>
<td>!140 KONNOV</td>
</tr>
</tbody>
</table>

**NH REACTIONS FROM ALLEN ET AL. COMB. FLAME 109, 449 (1997)**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Pre-Exp</th>
<th>E-Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH + O2 = HNO + O</td>
<td>3.89E+13</td>
<td>0.00</td>
<td>17890</td>
<td>!141</td>
</tr>
<tr>
<td>NH + O2 = HNO + O</td>
<td>7.60E+10</td>
<td>0.00</td>
<td>1530</td>
<td>!142 MERTENS, CHANG, HANSON, &amp; BOWMAN, IJCK, 23, 173, 1991</td>
</tr>
<tr>
<td>NH + O = NO + OH</td>
<td>5.50E+13</td>
<td>0.00</td>
<td>0</td>
<td>!143 MERTENS, CHANG, HANSON, &amp; BOWMAN, IJCK, 23, 173, 1991</td>
</tr>
<tr>
<td>NH + OH = HNO + H</td>
<td>2.00E+13</td>
<td>0.00</td>
<td>0</td>
<td>!144 MILLER &amp; BOWMAN, PROG. ENERGY COMBUST. SCI., 15, 287, 1989.</td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Preexponential Factor</td>
<td>Temperature</td>
<td>Reference</td>
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<tr>
<td>----------------------------------------------</td>
<td>---------------</td>
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<tr>
<td>NH + NO = N2O + H</td>
<td>3.13E+14</td>
<td>-0.45</td>
<td>0</td>
<td>MILLER AND MELIUS, 24TH INT. SYMP., COMB., 1992</td>
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<tr>
<td>NH + NO = N2 + OH</td>
<td>2.16E+13</td>
<td>-0.23</td>
<td>0</td>
<td>MILLER AND MELIUS, 24TH INT. SYMP., COMB., 1992</td>
</tr>
<tr>
<td>NH + NO2 = NO + HNO</td>
<td>1.00E+11</td>
<td>0.50</td>
<td>4000</td>
<td>CFM</td>
</tr>
<tr>
<td>NH + NH = N2 + H + H</td>
<td>5.10E+13</td>
<td>0.00</td>
<td>0</td>
<td>MILLER AND MELIUS, 24TH INT. SYMP., COMB., 1992</td>
</tr>
<tr>
<td>NH + O = HNO + H</td>
<td>6.63E+14</td>
<td>-0.50</td>
<td>0</td>
<td>MILLER &amp; BOWMAN, PROG. ENERGY COMBUST. SCI., 15, 287, 1989</td>
</tr>
<tr>
<td>NH2 + O = NH + OH</td>
<td>6.75E+12</td>
<td>0.00</td>
<td>0</td>
<td>MILLER &amp; BOWMAN, PROG. ENERGY COMBUST. SCI., 15, 287, 1989</td>
</tr>
<tr>
<td>NH2 + NO = NNH + OH</td>
<td>2.80E+13</td>
<td>-0.55</td>
<td>0</td>
<td>GLARBORG'S DENOX MECHANISM</td>
</tr>
<tr>
<td>NH2 + NO = N2 + H2O</td>
<td>5.16E+17</td>
<td>-1.82</td>
<td>0</td>
<td>GLARBORG'S DENOX MECHANISM (REFITTED FOR FORMAT CTI (A NEGATIF))</td>
</tr>
<tr>
<td>NH2 + NO = N2O + H2</td>
<td>5.00E+13</td>
<td>0.00</td>
<td>24640</td>
<td>CFM</td>
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<tr>
<td>NH2 + NO = HNO + NH</td>
<td>1.00E+13</td>
<td>0.00</td>
<td>4000</td>
<td>CFM</td>
</tr>
<tr>
<td>NH2 + NO2 = N2O + H2</td>
<td>3.28E+18</td>
<td>-2.20</td>
<td>0</td>
<td>MILLER &amp; BOWMAN, INT. J. CHEM. KINET., 23, 289, 1991</td>
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<tr>
<td>NH2 + NH = N2H2 + H</td>
<td>3.16E+13</td>
<td>0.00</td>
<td>994</td>
<td>HANSON</td>
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<tr>
<td>NH2 + NH = N2H2 + H2</td>
<td>3.98E+13</td>
<td>0.00</td>
<td>11922</td>
<td>HANSON</td>
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<tr>
<td>NH3 + OH = NH2 + H2</td>
<td>2.20E+16</td>
<td>0.00</td>
<td>93470</td>
<td>GLARBORG ET AL., INT. J. CHEM. KINET., 23, 289, 1991</td>
</tr>
<tr>
<td>NH3 + N2H2 + H</td>
<td>1.00E+13</td>
<td>0.00</td>
<td>0</td>
<td>GLARBORG ET AL., INT. J. CHEM. KINET., 23, 289, 1991</td>
</tr>
<tr>
<td>NH3 + OH = N2H2 + H2</td>
<td>2.04E+06</td>
<td>2.04</td>
<td>566</td>
<td>HANSON &amp; SALIMIAN, IN COMBUSTION CHEMISTRY, GARDINER, ED., SPRINGER-VERLAG, 1984.</td>
</tr>
<tr>
<td>NH3 + OH = N2H2 + H2</td>
<td>2.04E+06</td>
<td>2.04</td>
<td>566</td>
<td>GLARBORG ET AL., INT. J. CHEM. KINET., 23, 289, 1991</td>
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<tr>
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<td>2.04E+06</td>
<td>2.04</td>
<td>566</td>
<td>GLARBORG ET AL., INT. J. CHEM. KINET., 23, 289, 1991</td>
</tr>
<tr>
<td>NH3 + N2H2 + H</td>
<td>1.00E+13</td>
<td>0.00</td>
<td>22000</td>
<td>GLARBORG ET AL., INT. J. CHEM. KINET., 23, 289, 1991</td>
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<tr>
<td>NH3 + OH = N2H2 + H2</td>
<td>2.04E+06</td>
<td>2.04</td>
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<tr>
<td>NH3 + OH = N2H2 + H2</td>
<td>2.04E+06</td>
<td>2.04</td>
<td>566</td>
<td>GLARBORG ET AL., INT. J. CHEM. KINET., 23, 289, 1991</td>
</tr>
<tr>
<td>NH3 + OH = N2H2 + H2</td>
<td>2.04E+06</td>
<td>2.04</td>
<td>566</td>
<td>GLARBORG ET AL., INT. J. CHEM. KINET., 23, 289, 1991</td>
</tr>
<tr>
<td>NH3 + OH = N2H2 + H2</td>
<td>2.04E+06</td>
<td>2.04</td>
<td>566</td>
<td>GLARBORG ET AL., INT. J. CHEM. KINET., 23, 289, 1991</td>
</tr>
</tbody>
</table>
**N2H+H=N2+H2**  
1.00E+14 0.00 0 !170 GLARBORG ET AL., INT. J. CHEM. KINET., 26, 421, 1994.

**N2H+OH=N2+H2O**  
5.00E+13 0.00 0 !171 GLARBORG ET AL., INT. J. CHEM. KINET., 26, 421, 1994.

**N2H+NO=N2+HNO**  
5.00E+13 0.00 0 !172 MILLER & BOWMAN, PROG. ENERGY COMBUST. SCI., 15, 287, 1989.

**N2H+NH=N2+NH2**  
5.00E+13 0.00 0 !173 GLARBORG ET AL., INT. J. CHEM. KINET., 26, 421, 1994.

**N2H+NH2=N2+NH3**  
5.00E+13 0.00 0 !174 GLARBORG ET AL., INT. J. CHEM. KINET., 26, 421, 1994.

**N2H2=N2H2+N2**  
1.00E+13 0.00 9935 !175 HANSON

**N2H2+H=NNH+H2**  
1.00E+13 0.00 1987 !176 HANSON

**N2H2+NH=NNH+NH2**  
1.00E+13 0.00 0 !177 HANSON

**N2H2+M=NNH+H+M**  
1.00E+16 0.00 49675 !178 HANSON

**N2H2+M=NH+NH+M**  
3.16E+16 0.00 99350 !179 HANSON

**N2H2+N2H2=N2H4+NNH**  
1.00E+13 0.00 9935 !180 HANSON

**N2H2+O=NNH+OH**  
3.16E+11 0.50 0 !181 HANSON

**N2H2+OH=NNH+H2O**  
3.16E+11 0.50 0 !182 HANSON

**N2H2+O2=NNH+O2**  
3.16E+11 0.50 0 !183 HANSON

**N2H2+H=NNH+H2**  
1.00E+12 0.00 1987 !184 HANSON

**N2H2+NH=NNH+NH2**  
1.58E+12 0.00 0 !185 HANSON

**N2H2+M=NNH+H+M**  
1.00E+16 0.00 49675 !186 HANSON

**N2H2+M=NH+NH+M**  
3.16E+16 0.00 99350 !187 HANSON

**N2H3+H=N2H2+H2**  
1.00E+12 0.00 1987 !188 HANSON

**N2H3+H=N2H+H2**  
1.58E+12 0.00 0 !189 HANSON

**N2H3+H=NNH+H2**  
1.00E+11 0.00 0 !190 HANSON

**N2H3+N2H2=N2H4+NNH**  
2.50E+10 0.50 29805 !191 HANSON

**N2H3+O=N2H2+OH**  
3.16E+11 0.50 0 !192 HANSON

**N2H3+O=NNH+H2O**  
3.16E+11 0.50 0 !193 HANSON

**N2H3+OH=NNH+H2O**  
1.00E+13 0.00 1987 !194 HANSON

**N2H3+HO2=N2H2+H2O2**  
1.00E+13 0.00 1987 !195 HANSON

**N2H4+NH2=N2H3+NH3**  
3.98E+12 0.50 1987 !196 HANSON

**N2H4+H=N2H3+H2**  
1.29E+13 0.00 2503 !197 HANSON

**N2H4+H=NH2+H2**  
4.46E+09 0.00 3099 !198 HANSON

**N2H4+M=NH2+NH2+M**  
2.50E+10 0.50 29805 !199 HANSON

**N2H4+M=N2H3+H+M**  
6.31E+13 0.00 1192 !200 HANSON

**N2H4+OH=N2H3+H2O**  
2.51E+12 0.00 1192 !201 HANSON

**N2H4+OH=NNH+H2O2**  
3.98E+13 0.00 0 !202 HANSON

**N2H4+HO2=N2H3+H2O2**  
3.98E+13 0.00 1987 !203 HANSON

**NH+NO=O+NNH**  
1.85E+13 0.21 9931 !204 DEAN AND BOZZELI

!Begin OH* model******************************************************************************************************
H+O+M=OH*+M                              3.100E+14 0.0 10000
OH*+AR=OH+AR                                2.170E+10 0.5 2060
OH*+H2O=OH+H2O                                5.920E+12 0.5 -8.61E2
OH*+CO2=OH+CO2                                  2.750E+12 0.5 -9.68E2
OH*+CO=OH+CO                                   3.230E+12 0.5 -7.87E2
OH*+H2=OH+H2                                    2.950E+12 0.5 -4.44E2
OH*+O2=OH+O2                                   2.100E+12 0.5 -4.82E2
OH*+OH=OH+OH                                    1.500E+12 0.5 0.0
OH*+H=OH+H                                      1.500E+12 0.5 0.0
OH*+O=OH+O                                      1.500E+12 0.5 0.0
OH*+CH4=OH+CH4                                  3.360E+12 0.5 -6.35E2
OH*+N2=OH+N2                                    1.080E+11 0.5 -1238.0
OH*=OH+HV                                       1.400E+06 0.0 0.0
N2O+H=OH*+N2                                     1.60E+14 0.00 50300 ! 30 Hidaka J. phy. chem., 89, 4903

!End OH* model********************************************************************************

!CO2* Mechanism
CO+O+M<=>CO2(A)+M 4.0E+14 0.000 2.384E+03
H2/2.0/H2O/12/CO/1.75/CO2/3.6/AR/0.7/HE/0.7/
HCO+O<=>CO2(A)+H 3.000E+13 0.000 0.000E+00

!CO2* Quenching
CO2(A)+AR<=>CO2+AR                                8.421E+12 0.5 0.0
CO2(A)+H2O<=>CO2+H2O                                8.339E+12 0.5 0.0
CO2(A)+CO2<=>CO2+CO2                                 9.115E+12 0.5 0.0
CO2(A)+CO<=>CO2+CO                                   9.687E+12 0.5 0.0
CO2(A)+H<=>CO2+H                                     3.065E+13 0.5 0.0
CO2(A)+H2<=>CO2+H2                                    2.2710E+13 0.5 0.0
CO2(A)+O2<=>CO2+O2                                    8.774E+12 0.5 0.0
CO2(A)+O<=>CO2+O                                       9.819E+12 0.5 0.0
CO2(A)+OH<=>CO2+OH                                     9.872E+12 0.5 0.0
CO2(A)+CH4<=>CO2+CH4                                 1.190E+13 0.5 0.0
CO2(A)+N2<=>CO2+N2                                    9.963e12 0.5 0.0
CO2(A)<=>CO2+HV                                         1.000E+06 0.0 0.0

END

Thermodynamic Data

THERMO
300.000 1000.000 5000.000
H L 6/94H 1 0 0 0G 200.000 6000.00 1000.00 1
0.2500000000E+01 0.0000000000E+00 0.0000000000E+00 0.0000000000E+00 0.0000000000E+00 2

68
\[\begin{align*}
0.01664221E+06 &-0.04275205E+04 &0.03174204E+02 &0.01334867E+03 &3 \\
-0.01919685E+06 &0.07487564E+10 &0.01727270E+06 &0.07557224E+02 &4 \\
N2H4 &121286N &2H &4 &G &0.0000 &5000.00 &10000.00 &1 \\
0.04977317E+02 &0.09595519E-01 &0.03547639E-04 &0.06124299E-08 &0.04029795E-12 &2 \\
0.09341219E+05 &0.02962990E+12 &0.06442606E+01 &0.02749730E+00 &0.02899451E-03 &3 \\
0.01745240E-06 &0.04422282E-10 &0.01045192E+06 &0.02127789E+03 &4 \\
CO2(A) &L &7/88C &1O &2 &0 &0G &200.000 &6000.00 &10000.00 &1 \\
0.46365111E+01 &0.27414569E-02 &0.99589759E-06 &0.16038666E-09 &0.91619857E-14 &2 \\
-1.03030400E+03 &0.19348955E+01 &0.23568130E+01 &0.89841299E-02 &0.71220632E-05 &3 \\
0.24573008E-08 &0.14288548E-12 &3.73971000E+02 &0.99009035E+01 &0.47328105E+05 &4 \\
END
\end{align*}\]