QUANTIFYING NET HYDROXYL RADICAL CONSUMPTION FROM THE
OXIDATION OF VOLATILE ORGANIC COMPOUNDS AND SUBSEQUENT
OXIDATION PRODUCTS USING A POTENTIAL AEROSOL MASS CHAMBER

A Thesis in
Meteorology
by
Tiffany B. Samuelson

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The thesis of Tiffany B. Samuelson was reviewed and approved* by the following:

William H. Brune  
Distinguished Professor of Meteorology  
Head of the Department of Meteorology  
Thesis Advisor

Jose D. Fuentes  
Professor of Meteorology

Anne M. Thompson  
Professor of Meteorology

Johannes Verlinde  
Professor of Meteorology  
Associate Head, Graduate Program in Meteorology

*Signatures are on file in the Graduate School.
Abstract

The OH-initiated oxidation of volatile organic compounds (VOCs) begins a complex chain of chemical reactions that lead to a variety of products such as greenhouse gases, acids, other reactive species, and secondary organic aerosol. During these chemical processes, the VOC oxidation products will consume and produce additional OH radicals. Counting these OH radicals is uncertain, however, from explicit reaction mechanisms or direct constituent measurements alone. Therefore, a laboratory method is developed to count the average number of OH radicals consumed or produced by the oxidation of VOCs and subsequent reaction products in the highly oxidizing environment of a Potential Aerosol Mass chamber. The amount of OH consumed is determined by first creating an OH exposure calibration curve relating OH exposure to the number of OH radicals consumed using carbon monoxide (CO). Carbon monoxide is an ideal calibration gas because only one OH radical is consumed per reaction, and its reaction products, carbon dioxide (CO$_2$) and hydrogen (H), are unlikely to have a large impact on the number of OH radicals. Then, OH exposure is measured for a VOC over a range of mixing ratios. Finally, the net number of OH radicals consumed or produced by the VOC is estimated by comparing the VOC OH exposure curve to the calibration curve.

This technique is applied to several relevant atmospheric VOCs: propane, isoprene, m-xylene, and α-pinene. These experiments suggest that propane and its oxidation products may consume between 1.2 and 2.9 OH radicals per VOC molecule consumed, isoprene between 2.1 and 12.5 OH radicals, m-xylene between 2.3 and 20.7 OH radicals, and α-pinene between 1.6 and 6.5 OH radicals per VOC molecule oxidized, over a range of VOC mixing ratios from 0 to 650 ppb. These results, however, are found to be dependent upon certain initial conditions and the initial amount of VOC added, the number of OH radicals consumed decreasing as the amount of VOC added increases and OH exposure decreases. The OH counting over atmospherically
relevant VOC mixing ratios is in an experimental range of reduced sensitivity and large uncertainties which may limit the applicability of this method to the atmosphere.

Theoretical and modeling efforts are also employed to estimate the number of OH radicals consumed per VOC molecule oxidized. Theoretical OH counting estimated from reaction mechanisms in relevant literature finds that propane and its oxidation products consume approximately 1.8 OH radicals per VOC molecule oxidized, isoprene 2.3 OH radicals, m-xylene 3.5 OH radicals, and α-pinene 1.9 OH radicals per VOC molecule oxidized. Simple modeled predictions of OH counting, however, significantly overestimate the theoretical and experimental number of OH radicals consumed per VOC molecule oxidized by approximately a factor of 1.1 to 4.3, except for one case with m-xylene. Enhanced modeling efforts may be necessary to capture the OH counting method implemented in the PAM chamber.
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<th>Description</th>
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<tbody>
<tr>
<td>ΔCO</td>
<td>Number of CO Molecules Consumed</td>
</tr>
<tr>
<td>ΔCO/ΔVOC</td>
<td>Number of OH Radicals Consumed per VOC molecule oxidized</td>
</tr>
<tr>
<td>ΔOH</td>
<td>Number of OH Radicals Consumed</td>
</tr>
<tr>
<td>ΔO₃</td>
<td>Number of O₃ Molecules Consumed</td>
</tr>
<tr>
<td>ΔVOC</td>
<td>Number of VOC Molecules Consumed</td>
</tr>
<tr>
<td>GC-FID</td>
<td>Gas Chromatograph with Flame Ionization Detector</td>
</tr>
<tr>
<td>PAM</td>
<td>Potential Aerosol Mass</td>
</tr>
<tr>
<td>ppb</td>
<td>Parts Per Billion</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts Per Million</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary Organic Aerosol</td>
</tr>
<tr>
<td>TPOT</td>
<td>Toronto Photo-Oxidation Tube</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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# Chemical Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>CH₂</td>
<td>Methylene Group</td>
</tr>
<tr>
<td>CH₃</td>
<td>Methyl Group</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>C₃H₇</td>
<td>Propyl Radical</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>Propane (CH₃CH₂CH₃)</td>
</tr>
<tr>
<td>C₅H₈</td>
<td>Isoprene (CH₂=C(CH₃)CH=CH₂)</td>
</tr>
<tr>
<td>C₆H₁₂</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>C₈H₁₀</td>
<td>m-xylene</td>
</tr>
<tr>
<td>C₁₀H₁₆</td>
<td>α-pinene</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HOCO</td>
<td>Hydroxyformyl Radical</td>
</tr>
<tr>
<td>HOSO₂</td>
<td>Hydroxysulfonyl Radical</td>
</tr>
<tr>
<td>HO₂</td>
<td>Hydroperoxy Radical</td>
</tr>
<tr>
<td>HOₓ</td>
<td>Hydrogen Oxides (OH + HO₂)</td>
</tr>
<tr>
<td>H₂</td>
<td>Molecular Hydrogen</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Hydrogen Peroxide</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sulfuric Acid</td>
</tr>
<tr>
<td>hν</td>
<td>Photochemical Energy</td>
</tr>
<tr>
<td>M</td>
<td>Air Molecule</td>
</tr>
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</table>
N₂  Molecular Nitrogen
NO  Nitric Oxide
NOₓ  Nitrogen Oxides (NO + NO₂)
O(^1D)  Excited State Atomic Oxygen
O(^3P)  Ground State Atomic Oxygen
OH  Hydroxyl Radical
O₂  Molecular Oxygen
O₃  Ozone
R  Alkyl Radical
R"  Alkyl Radical (Alternate Structure)
R’CHO  Carbonyl
RH  Organic Compound
RO  Alkoxy Radical
R’O  Alkoxy Radical (Alternate Structure)
RO₂  Organic Peroxy Radical
R’O₂  Organic Peroxy Radical (Alternate Structure)
ROH  Alcohol
ROOH  Hydroperoxide
ROOR  Organic Peroxide
SO₂  Sulfur Dioxide
SO₃  Sulfur Trioxide
X  A Precursor Gas
Acknowledgements

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Chapter 1
INTRODUCTION

Although the importance of the hydroxyl (OH) radical in the troposphere is well-understood, the factors regulating the atmospheric lifetime, interactions, distribution, and reaction products of the OH radical are not yet concrete. The OH radical reacts with and is the dominant loss mechanism for almost all organic atmospheric species. Of these organic atmospheric species, volatile organic compounds (VOCs) are an important class emitted by biogenic and anthropogenic processes (Atkinson and Arey 2003; Guenther et al. 1995; Logan et al. 1981). When an OH radical reacts with a VOC, this oxidation process initiates a complex chain of atmospheric reactions that lead to a variety of pollutants. These pollutants include greenhouse gases such as carbon dioxide (CO₂) and potentially harmful ozone (O₃), acids, other reactive oxygenated VOCs, and particulates, known as secondary organic aerosol (SOA) (Kroll and Seinfeld 2008).

The complexity of these reaction chains and the high variability of atmospheric conditions make predicting and understanding the minutiae of these OH-initiated chemical mechanisms difficult. In order to understand these mechanisms and their impact, numerous studies have been conducted using in situ, satellite, modeling, theoretical, and laboratory-based methods with some success. Often, though, measurements cannot be reconciled to theoretical and modeling estimates. These discrepancies are also observed in estimating the total impact of VOC reactions on the OH radical. After the initial reaction between a VOC and an OH radical, the reaction products continue to interact with the OH radical, leading to additional consumption and production of OH radicals through various reaction pathways. The net impact on the OH radical,
however, is difficult to deduce from theoretical reaction mechanisms or direct measurements alone.

Recent scientific advances have introduced methods of measuring and studying OH radical reactions in the atmosphere, such as OH reactivity and direct measurement techniques. For instance, direct measurements of the OH and hydroperoxyl (HO₂) radicals are possible with laser-induced fluorescence at low pressures in an evacuated detection chamber in the Ground and Airborne-based Tropospheric Hydrogen Oxides Sensor (Brune et al. 1995; Faloona et al. 2004). Furthermore, Kovacs and Brune (2001) also develops an instrument for the direct measurement of total OH reactivity in the air using a discharge flow technique and laser-induced fluorescence. This instrument has been used to explore OH reactivity in many campaigns in a variety of environments (Carroll et al. 2001; Di Carlo et al. 2004; Kovacs and Brune 2003), often in conjunction with the aforementioned direct OH radical sensor (Mao et al. 2009, 2010; Ren et al. 2003, 2005, 2006; Shirley et al. 2006).

Sinha et al. (2008) introduces a comparative OH reactivity method to measure the total loss rate of OH radicals in a glass reactor by first introducing a certain amount of a reactive molecule. By comparing the amount of this molecule consumed in the presence of OH radicals to the amount consumed in the presence of both OH radicals and an air sample, the OH reactivity in the sample air can be quantified. While both OH reactivity and direct measurements are useful methods of studying atmospheric OH radical interactions, the impact of individual VOCs on these measurements is often difficult to deduce from these types of studies. Therefore, controlled, laboratory-based experiments are more useful in exploring how unique VOCs interact with the OH radical.

In a laboratory setting, other metrics, such as OH exposure, can be used as a measurement of OH radicals in a system, often more reliably than direct measurements. The OH exposure is a measure of the concentration of OH radicals over a period of time and therefore an indicator of the level of OH radicals present. While a VOC and its oxidation products are in the
system, these species will consume a certain number of OH radicals, resulting in a particular concentration of OH radicals and OH exposure over that period of time.

The measurement of OH exposure is a particularly useful metric for indicating the level of OH radicals in a controlled environment. Environmental chambers provide a means of controlling ambient conditions, such as relative humidity, temperature, and chemical constituents, making environmental chambers valuable resources for simulating atmospheric chemical reactions. These chemical reactions, however, often take days to weeks to progress in the atmosphere; therefore, environmental chambers can introduce high levels of atmospheric oxidants to speed up naturally occurring oxidation reactions under controlled conditions. The Potential Aerosol Mass (PAM) chamber is a highly oxidizing environmental chamber designed with a small volume and short residence time to accelerate atmospheric chemical reactions. The PAM chamber, therefore, is an ideal environment for the measurement of OH exposure.

This research introduces a new laboratory-based method for counting the net number of OH radicals consumed or produced by the oxidation of individual atmospheric VOCs and subsequent reaction products. This OH counting method is based on finding a relationship between OH exposure and the net number of OH radicals consumed by a precursor gas. This relationship is determined by first creating an OH exposure calibration curve by measuring the OH exposure for a calibration gas in the highly oxidizing environment of the PAM chamber. This calibration gas must be a direct indicator of the number of OH radicals consumed by that gas. An OH exposure curve is then created for an applicable atmospheric VOC. By comparing the VOC OH exposure curve to the OH exposure calibration curve, the average number of OH radicals consumed or produced by the VOC and subsequent oxidation products is measured. This technique can be applied to a suite of atmospheric VOCs to create a profile of the impact on the OH radical. This study will test the OH counting method on four relevant VOCs: propane, isoprene, m-xylene, and α-pinene.
The ability to count the number of OH radicals consumed or produced by these unique chemical species and subsequent reaction products has important implications for modeling OH interactions in the atmosphere. The OH counting method provides another way of studying OH reactivity and a basis for improving our understanding of individual OH-initiated chemical mechanisms for further constraint of chemical models. These OH interactions are important to understand because the resulting pollutants described, especially SOA, have been shown to have a strong impact on air quality, human health, visibility, cloud formation, and the global climate. Therefore, gaining insight on how to further constrain these atmospheric processes in models will greatly improve the information available for air quality forecasting and policy and decision-making.
Chapter 2

BACKGROUND

The OH radical is fundamental to understanding tropospheric chemistry and is the dominant loss mechanism for most trace chemical species in the atmosphere. Therefore, an outline of the complex OH chemistry with VOCs is detailed in Section 2.1. This same chemistry is also present in the PAM chamber and is important to the OH counting method introduced. Therefore, the theoretical basis and chemical applications of the OH counting method are also described in this chapter.

2.1 The Atmospheric Chemistry

These experiments will make use of the simulated atmosphere of the PAM chamber to create a low NOx environment to test the OH counting method. In the absence of NOx, the following well-understood HOx reactions in Figure 2.1 will dominate the chemistry. The PAM concept is designed for extremely high amounts of these atmospheric oxidants, including OH, HO2, and O3. Therefore, the impact of VOCs on the cycling between these oxidants creates the basis for the OH counting method.

The OH radical is the dominant oxidant for most atmospheric VOCs, including hydrocarbons. When such an organic species (RH) is introduced to the atmosphere during the daytime, this radical is likely to react with the OH radical and form organic peroxy radicals (RO2) via the following reaction mechanisms with the OH radical and then oxygen (O2):

\[
RH + OH \rightarrow R + H_2O \tag{R1}
\]

\[
R + O_2 + M \xrightarrow{fast} RO_2 + M \tag{R2}
\]
where an alkyl radical (R) is produced from the initial OH attack. The R then reacts rapidly with O₂ to form an RO₂. This created RO₂ will react with either the HO₂ radical or another RO₂ (R’O₂) in self-reactions (RO₂ + RO₂) or cross-reactions (RO₂ + R’O₂) which proceed through similar reaction mechanisms described in (R7) through (R9). The prime (’) indicates a similarly behaving molecule with a different structure. The dominance of each pathway, however, varies by chemical species. The four possible reaction paths for RO₂ + HO₂ result in the production of organics, such as hydroperoxides (ROOH) in (R3), carbonyls (R’CHO) in (R4), alcohols (ROH) in (R5), or alkoxy radicals (RO) in (R6). These RO₂ self and cross-reactions also result in a variety of organics, including alkoxy radicals, RO and R’O, in (R7), ROH and R’CHO in (R8), or organic peroxides (ROOR) in (R9) (Hasson et al. 2004; Kroll and Seinfeld 2008).

\[
RO₂ + HO₂ \rightarrow ROOH + O₂ \quad (R3)
\]

\[
\rightarrow R’CHO + H₂O + O₂ \quad (R4)
\]

\[
\rightarrow ROH + O₃ \quad (R5)
\]

\[
\rightarrow RO + OH + O₂ \quad (R6)
\]
Among these reactants, the RO radical also has three dominant pathways that can lead to the regeneration of R and RH. The dissociation reaction of RO in (R10) results in the formation of an R’CHO and an alkyl radical (R’’). Reaction (R11) is an isomerization reaction, or a hydrogen atom shift from one position on the molecule to another in RO, that results in the formation of a hydroxyalkyl radical (R’_OH). Reaction (R12) between RO and O_2 produces an R’CHO and HO_2. These RO and RO_2 reaction products in (R3) through (R12) will continue to react with various oxidants, particularly OH, O_3, O_2, and HO_2. These reactions can lead to the formation of high volatility products, such as CO_2 or formaldehyde (CH_2O), or lower volatility products that may result in aerosol formation. Alternatively, these products may also be photolyzed or removed by an external deposition process. (Kroll and Seinfeld 2008; Molina et al. 2004).

\[
RO \rightarrow R'CHO + R'' \quad (R10)
\]

\[
R'OH \quad (R11)
\]

\[
RO + O_2 \rightarrow R'CHO + HO_2 \quad (R12)
\]

Reactions (R1) through (R12) describe the general gas-phase evolution of VOCs in the atmosphere initiated by OH radical oxidation, but these reactions can also lead to the formation of particles known as secondary organic aerosol (SOA). The oxidation of VOCs often leads to lower volatility and increasingly oxidized products that can thereafter partition into the condensed phase and form particulate matter. For instance, the ROOH produced in (R3) by the reaction between RO_2 and HO_2, is of lower volatility than the initial VOC and is thought to be a significant source of SOA. Similarly, ROOR in (R9) is also thought to be a source of SOA, though its significance is much less certain. Furthermore, the subsequent isomerization of R’_OH can lead to lower
volatility products such as hydroxycarbonyls, polyols, and dihydrofurans (Kroll and Seinfeld 2008). Dissociation reactions, on the other hand, cleave the carbon structure of the molecule, often creating more volatile compounds. Through these chemical mechanisms, the SOA created is generally a conglomeration of compounds in multiple phases that are subject to continual physical and chemical processes in the atmosphere.

The atmospheric evolution of SOA, or aging, is the subject of much recent study because aerosol have been shown to have a strong impact on human health, visibility, cloud formation, and the climate and are a significant portion of particulate matter globally. Aerosol can have atmospheric lifetimes on the order of days to weeks, during which they undergo continuous physical and chemical aging processes. The OH radical is also an active participant in these chemical aging processes, converting low-volatility products into SOA and affecting the coexistence of the phases present, or gas-particle partitioning, in semi-volatile organic compounds.

The aging of SOA can be described by three mechanisms: functionalization, fragmentation, and oligomerization. Functionalization refers to the addition of oxygenated functional groups to a molecule without changing the amount of carbon. This mechanism generally results in lower volatility products and thus a greater likelihood of partitioning into the aerosol phase. Fragmentation refers to the cleavage of carbon-carbon bonds which can result in either higher or lower volatility products (Donahue et al. 2006; Henry and Donahue 2012). Oligomerization refers to condensed phase reactions that result in products with greater carbon and oxygen numbers and decreased vapor pressure (Rudich et al. 2007). A study of α-pinene SOA in the Carnegie Mellon Smog Chamber by Henry and Donahue (2012) verifies that higher concentrations of the OH radical lead to greater functionalization, lower volatility groups, and more SOA. Lower concentrations of the OH radical, on the other hand, favor fragmentation and the photolysis and evaporation of highly functionalized groups. Therefore, the atmospheric SOA depends critically on the balance of photolysis and the reactions with the OH radical.
Because the reaction mechanisms of VOCs and any subsequent reaction products are so complex beyond the initial OH attack, the gas and particle phase evolution of these chemical species, as well as their impact on the oxidizing species, is very uncertain and the subject of ongoing study. From the reaction mechanisms described in (R1) through (R12) and subsequent evolution of these species in the atmosphere, it is evident that OH radical interactions with VOCs are important not only to these gas and particle phase species, but also to the lifetime and distribution of the OH radical. The various mechanisms described lead to the further consumption and production of the OH radical in the atmosphere; therefore, the OH counting method will help to quantify the effect of these mechanisms on the OH radical. Quantifying this impact for individual VOCs is useful because this additional OH consumption or production is highly variable by the type of VOC and ambient environmental conditions.

Forms of OH radical counting have been explored in previous studies, particularly in quantifying the yield of OH radical production from the ozonolysis of alkenes and other atmospheric species. Atkinson et al. (1992), Atkinson and Aschmann (1993), and Aschmann et al. (1996) carry out experiments in a Teflon environmental chamber to quantify the yield of OH radical production from alkenes and other VOCs using cyclohexane (C₆H₁₂) as an OH scavenger. Alvarado et al. (1998) and Aschmann et al. (2002) use a similar technique with 2-butanol as a scavenger, while Rickard et al. (1999) uses 1,3,5-trimethylbenzene and Paulson et al. (1999) uses a small-ratio relative rate technique. These works find that the yield of OH formation can range from 0.08 to 1.15 for these select alkenes. Similarly, OH formation yields are also estimated for the ozonolysis of olefins by laser-induced fluorescence techniques in Donahue et al. (1998) and Kroll et al. (2002). The yield of OH formation from the ozonolysis of isoprene, for instance, has also been studied using theoretical product and kinetic studies (Gutbrod et al. 1997; Zhang and Zhang 2001; Zhang et al. 2002); similar analyses have also been performed for most relevant atmospheric VOCs.
Although these studies recognize the importance of the production of reactive oxidation products, they do not seek to completely characterize the OH radical interactions by neglecting all OH radical reactions that may occur after the initial OH production. In fact, there are very few estimates in the literature that attempt to assess the number of OH radicals that may be consumed or produced by the oxidation of a reactive species. Japar et al. (1990) attempts simple estimates of the number of OH radicals consumed by a variety of ethers used as fuel additives; these estimates, however, are based solely on very limited theoretical mechanisms. Therefore, this work introduces a laboratory-based OH counting method to further constrain the impact of VOCs on the production and consumption of OH radicals in the PAM chamber.

2.2 Theoretical Basis for the OH Counting Method

The chemical processes described in Section 2.1 introduce the atmospheric interactions between the OH radical and VOCs. Because of this complex chemistry, the net impact of these interactions on the OH radical is uncertain from the reaction mechanisms alone. Therefore, a laboratory-based method of counting the net number of OH radicals consumed or produced through these reactions is introduced in this section. This method of counting OH radicals is based on the idea that the number of OH radicals consumed by a precursor gas can be estimated by relating OH exposure to the number of OH radicals consumed (molecules cm\(^{-3}\)). The OH exposure is defined in equation (1) as the concentration of OH integrated over time in units of molecules cm\(^{-3}\) s.

\[
\text{OH exposure} = \int [OH] \, dt
\]  

(1)

The OH exposure is a measure of the amount of OH radicals present and also an indicator of how quickly precursor gases and subsequent reaction products are oxidized by the OH radical (Kang et al. 2011).
This OH counting method is implemented by first creating an OH exposure calibration curve relating OH exposure to the number of OH radicals consumed by a calibration gas. This OH exposure calibration curve, hereafter referred to as the calibration curve, is created using a calibration gas for which the amount of OH radicals consumed in a reaction is known. Carbon monoxide is selected as the calibration gas and is ideal for this application for several reasons that are discussed in Section 2.4. The calibration curve is constructed by measuring OH exposure in the PAM chamber for a range of CO concentrations. When varying the amount of CO added to the system, different amounts of CO are consumed at different CO concentrations, changing both the number of OH radicals consumed and the OH exposure. Because one CO molecule and one OH radical are consumed in a reaction, the number of CO molecules consumed is equal to the number of OH radicals consumed; therefore, the calibration curve represents the number of OH radicals consumed as a function of OH exposure in the PAM chamber.

An OH exposure curve can also be constructed for other precursor gases, such as VOCs. A VOC OH exposure curve is constructed by measuring the OH exposure for a range of VOC concentrations. The VOC OH exposure values represent the actual number of OH radicals consumed by that VOC and subsequent reaction products, whereas the calibration curve represents the number of OH radicals consumed by initial reactions alone. Comparing the VOC OH exposure curve to the calibration curve indicates how many additional OH radicals are either consumed or produced in reactions with the subsequent reactions products. Furthermore, the number of OH radicals consumed by the VOC and subsequent reaction products per VOC molecule oxidized is determined by dividing the ∆OH values on the calibration curve (ΔCO) by the values on each VOC OH exposure curve (ΔVOC) at corresponding OH exposures. This OH counting method is a useful technique to apply to VOCs because the OH radical is the dominant loss mechanism for most atmospheric VOCs (Guenther et al. 1995). Therefore, other chemical species in the chamber are unlikely to react significantly with the added VOC. Some VOCs,
however, also react with O$_3$, though much more slowly than reactions with the OH radical. Thus, interactions with the OH radical still dominate the processes in the PAM chamber.

According to this theory, OH exposure curves are constructed for a calibration gas and applicable VOCs. Figure 2.2 illustrates the application of the OH counting method with an idealized calibration gas and two different, unspecified VOCs. The VOC OH exposure curve represents the actual number of OH radicals consumed by the initial VOC and the concentration of OH radicals present under those conditions. The number of OH radicals consumed ($\Delta$OH) is directly inferred from the amount of the VOC consumed ($\Delta$VOC) because one VOC molecule will consume one OH radical in the initial reaction. Therefore, for a VOC OH exposure curve, $\Delta$OH is equal to $\Delta$VOC. The calibration curve, on the other hand, represents the number of OH radicals that would be required to consume that many VOC molecules if there were no other reactions occurring to consume or produce additional OH radicals in the chamber.

![Graph](image)

**Figure 2.2** Idealized OH exposure curves for the calibration gas (blue diamond) and unspecified VOCs (orange square and green triangle).
For instance in Figure 2.2, if 4 x 10^{12} molecules cm^{-3} of VOC A is added to the chamber, an OH exposure of 8 x 10^{11} molecules cm^{-3} s is measured. At this OH exposure, the calibration curve indicates that 8 x 10^{12} molecules cm^{-3} of VOC A would have to be present in the chamber to consume that many OH radicals by initial reactions with the VOC alone. Therefore, in the case of VOC A, 4 x 10^{12} molecules cm^{-3} more OH radicals are being consumed than what is predicted by the calibration curve, and the additional 4 x 10^{12} molecules cm^{-3} of OH radical consumption is from the VOC A oxidation products. These curves also indicate that 2.0 OH radicals are consumed by VOC A and subsequent reaction products per VOC A molecule oxidized, meaning that VOC A oxidation products consume 1.0 additional OH radical. This conclusion can also be explained in Figure 2.2 by considering that OH exposure is an indicator of the concentration of OH radicals in the chamber, therefore, the greater the OH exposure, the more OH radicals there are present in the chamber. The OH exposure curve for VOC A indicates that 4 x 10^{12} molecules cm^{-3} of OH radical consumption is associated with an OH exposure of 8 x 10^{11} molecules cm^{-3} s. The calibration curve, on the other hand, indicates that 4 x 10^{12} molecules cm^{-3} of OH radical consumption is associated with an OH exposure of 10 x 10^{11} molecules cm^{-3} s when no other OH radical reactions are occurring in the chamber. Thus, the calibration curve indicates that there would be higher levels of OH radicals present, and higher OH exposures, in the chamber if there were no other reactions occurring to consume additional OH radicals. Therefore, similar conclusions can be drawn by comparing the ΔOH at the same OH exposures or the OH exposure at the same ΔOH.

Similarly, if 12 x 10^{12} molecules cm^{-3} of VOC B is added to the system, an OH exposure of 8 x 10^{11} molecules cm^{-3} s is measured in the chamber. At this OH exposure, the calibration curve indicates that only 8 x 10^{12} molecules cm^{-3} of VOC B would have to be present in the system to consume that many OH radicals by initial reactions alone. Therefore, in the case of VOC B, 4 x 10^{12} molecules cm^{-3} more OH radicals are being produced by reactions with the VOC oxidation products. Similarly, 0.67 OH radicals are consumed by VOC B and subsequent reaction
products per VOC B molecule oxidized, and 0.33 OH radicals are produced by VOC B oxidation products.

Finally, in the unique case that a VOC OH exposure curve is identical to the calibration curve, the OH consumption by that VOC would be 1.0 OH radicals per VOC molecule oxidized. In that event, these results would indicate that subsequent oxidation products, overall, consume and produce the same amount of OH radicals so that any additional OH consumption by the VOC oxidation products cancels out. Else, the VOC may also have a very similar oxidation mechanism to the calibration gas that results in similar OH consumption.

2.3 OH Exposure as an Indicator of OH Consumption

The OH counting method uses OH exposure to indicate how many OH radicals are in the PAM chamber under any conditions, and assuming the production of OH radicals remains constant, OH exposure can also indicate how many OH radicals have been consumed. Considering the general rate equation for the OH radical in equation (2), the time rate of change of [OH] is defined by its production ($P_{OH}$) minus its losses due to the HO$_x$ chemical mechanisms ($L[OH]_{HO_x}$) described in Section 2.1 and losses due to other precursor gases ($L[OH]_{precursor}$), such as VOCs.

$$\frac{d[OH]}{dt} = P_{OH} - L_{HO_x}[OH] - L_{precursor}[OH] \approx 0$$

(2)

Because the OH radical is highly reactive and short-lived, the [OH] rate term can be approximated as zero. By making this assumption and solving for [OH], [OH] becomes the ratio of its production to its losses by HO$_x$ mechanisms and other precursors in equation (3). This idea can then be substituted into the OH exposure equation introduced in equation (1).

$$[OH] = \frac{P_{OH}}{L_{HO_x} + L_{precursor}}$$

(3)
\[ \text{OH exposure} = \int [OH] dt = \int \frac{P_{OH}}{L_{HO_x} + L_{\text{precursor}}} \, dt \quad (4) \]

The conditions in the PAM chamber are such that the ratio of OH production to losses due to HO\(_x\) chemistry remain relatively constant because the most significant source of the OH radical is from the mechanism initiated by the photolysis of O\(_x\) and losses are always proportional to the concentration of OH radicals produced. Therefore, OH exposure is significantly dependent upon the loss of OH radicals to other precursor gases or products that may consume OH radicals in the PAM chamber, such as VOCs, CO, oxidation products, and aerosol. Adding and producing varying amounts of these precursor gases and products will change the OH exposure by a unique amount. In this way, OH exposure can be used as an indicator of OH consumption in the PAM chamber.

2.4 CO as a Calibration Gas

The calibration gas is selected to be CO because it reacts with the OH radical in the following manner:

\[ \text{CO} + \text{OH} \leftrightarrow \text{HOCO} \rightarrow \text{CO}_2 + \text{H} \quad (R13) \]

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad (R14) \]

where HOCO is a possible intermediary product that instantaneously collapses to CO\(_2\) and hydrogen (H). Carbon monoxide is an ideal candidate for creating an OH exposure calibration curve for several reasons.

1. One CO molecule is consumed for each OH radical consumed in a chemical reaction; therefore, the number of OH radicals consumed is inferred directly from the measured amount of CO consumed.
(2) In the PAM chamber, CO does not react significantly with any other species present; therefore, the OH radical is the dominant loss mechanism for CO in the chamber, similar to the atmosphere (Logan et al. 1981).

(3) The products of reactions (R13) and (R14) are unlikely to consume additional OH radicals which may alter the measurement of OH exposure. Specifically, CO$_2$ is nonreactive with OH, and the H reacts rapidly with O$_2$ to form HO$_2$. The production of HO$_2$, however, does lead to the production and consumption of additional OH radicals by the HO$_x$ reaction mechanisms described in Figure 2.1. The impact of OH recycling on the construction of the calibration curve and OH counting is discussed in greater detail in Section 4.2.

(4) Carbon monoxide has well-established, accessible, and accurate monitoring devices.

2.5 Description of Chemical Species

This theory will be tested on four relevant atmospheric VOCs. These VOCs are selected from a variety of molecular complexities, carbon numbers, and from both anthropogenic and biogenic sources. Figure 2.3 illustrates the chemical configurations of these four VOCs: propane, isoprene, $m$-xylene, and $\alpha$-pinene. The dominant loss mechanism for all of these VOCs is the OH radical, and atmospheric lifetimes are on the order of hours for the more complex molecules (Guenther et al. 1995; Zalel et al. 2008) and on the order of days to weeks for propane (Rosado-Reyes and Francisco 2007). Typical atmospheric mixing ratios range from several tens to several hundred ppb (Martin et al. 1991; Panthak et al. 2007; Rosado-Reyes and Francisco 2007; U.S. Dept. of Health and Human Services 2007).

In the absence of NO$_x$, OH radical interactions with VOC oxidation products are likely significant, particularly for the more complex molecules, isoprene, $m$-xylene, and $\alpha$-pinene. Common to these more complex molecules is existing evidence that their photooxidation products result in the formation of SOA (Claeys et al. 2004; Forstner et al. 1997; Kavouras et al. 2016).
Studies have also shown that SOA production from these chemical species is NOₓ dependent, SOA production increasing as NOₓ levels decrease (Hatakeyama et al. 1991). The oxidation of propane, however, is much less likely to result in SOA production because SOA yields decrease with decreasing length of the parent molecule carbon chain (Aumont et al. 2012).

Propane is an alkane that is emitted into the atmosphere from both anthropogenic and biogenic sources at a rate of approximately 15 to 20 Tg yr⁻¹. Sources include biomass burning, manufacturing processes, volcanoes, microbes, and losses of fuels, including natural gas, gasoline, and diesel (Singh et al. 1994). The kinetics of the reaction between propane and the OH radical proceed at a rate of 1.1 x 10⁻¹² cm³ molecules⁻¹ s⁻¹ at 298 K (Sander et al. [NASA JPL Eval. No. 17], 2011), and the OH radical is the dominant loss mechanism for propane in the atmosphere. Propane reacts with the OH radical by H-abstraction from any of the methyl (CH₃) or methylene (CH₂) groups to form the propyl radical (C₃H₇). Depending upon the site of the H-abstraction, two isomers of the propyl radical can be formed: i-C₃H₇ (CH₃CHCH₃, 80%) or n-C₃H₇ (CH₂CH₂CH₃, 20%) that have the potential to lead to the formation of different products under certain atmospheric conditions (Singh et al. 1994).

Isoprene, or 2-methyl-1,3-butadiene, is a terpene that is emitted by vegetation, especially tropical rainforests, at a rate of approximately 410 Tg yr⁻¹ (Müller et al. 2008). Isoprene is one of the most important natural sources of VOCs, representing 44% of total natural VOC emissions

![Chemical configurations of atmospheric VOCs](image)

**Figure 2.3** Chemical configurations of atmospheric VOCs to be tested with OH counting method.
The rate constant for the reaction between isoprene and the OH radical is $1.0 \times 10^{10}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at 298 K. While OH-initiated oxidation is the dominant sink for isoprene in the atmosphere, isoprene also reacts with O$_3$ with a rate constant of $1.3 \times 10^{17}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at 298 K (Atkinson et al. 2006). The OH radical attacks isoprene almost entirely by OH-addition, adding an OH to any of four possible locations on the double carbon bonds. Approximately 90% of the OH-additions, however, occur near the CH$_2$ groups (Fan and Zhang 2004).

$m$-Xylene is an aromatic VOC commonly emitted in industrial and combustion processes such as fuel combustion and evaporation (Bailey et al. 1990). The dominant loss mechanism for $m$-xylene in the atmosphere is oxidation by the OH radical with a rate constant of $2.3 \times 10^{11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at 298 K (Atkinson and Arey 2003). $m$-Xylene, however, reacts much more slowly with O$_3$, the kinetics of this reaction proceeding slow enough to be neglected in these experiments (Kramp and Paulson 1998). The initial reaction between the OH radical and $m$-xylene proceeds by H-abstraction from a methyl group (10%) or by OH-addition to form a dimethylhydroxycyclohexadienyl radical (90%) (Zhao et al. 2005).

$\alpha$-Pinene is a monoterpene and biogenic VOC that is most recognizable as an emission from pine trees and other vegetation. Monoterpenes represent 11% of the total natural VOC emissions annually, $\alpha$-pinene being the dominant monoterpene species (Guenther et al. 1995). The dominant loss mechanism for $\alpha$-pinene in the atmosphere is the OH radical with a rate constant of $5.3 \times 10^{11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at 298 K, but $\alpha$-pinene also reacts with O$_3$ with a rate constant of $9.0 \times 10^{17}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at 298 K (Atkinson et al. 2006). $\alpha$-Pinene reacts with the OH radical by either H-abstraction (12%) or by OH-addition (88%) (Capouet et al. 2004). A summary of the relevant reaction rate coefficients in the implementation of the OH counting method is located in Chapter 5 in reference to modeling efforts.

The OH counting method is complicated by the ozonolysis of isoprene and $\alpha$-pinene. Therefore, the VOC oxidation, or $\Delta$VOC, cannot be entirely attributed to oxidation by the OH
radical. This effect is small for the conditions present in the PAM chamber because OH radical chemistry dominates the reactions. This method is further complicated because OH radicals are also likely formed from the ozonolysis of VOCs, particularly terpenes, monoterpenes, and other alkenes (Aschmann et al. 2002; Gutbrod et al. 1996; Paulson et al. 1999). Studies compared by Paulson et al. (1999) indicate that O$_3$-initiated oxidation of isoprene leads to the production of the OH radical at a yield of approximately 0.3, while O$_3$-initiated oxidation of $\alpha$-pinene leads to the production of the OH radical at a yield of approximately 0.8. Because only a small portion of the VOC added will be consumed by O$_3$ under these experimental conditions, this OH production from VOC ozonolysis is likely not significant. The impact of ozonolysis on the application of the OH counting method is discussed in more detail and quantified in Chapter 4.
Chapter 3

EXPERIMENTATION

The OH counting method described in Chapter 2 will be executed using the PAM chamber and instrumentation described in Section 3.1. The experimental procedure and monitoring gas used to measure OH exposure for the calibration gas and VOCs are also explained in this chapter.

3.1 The PAM Chamber and Instrumentation

The OH counting method will be tested by laboratory-based experiments using a PAM chamber. The PAM concept was first developed by researchers at the Pennsylvania State University as a Teflon flow reactor (Kang et al. 2007). The PAM chamber has since been modified to an aluminum, flow-through chamber with a short residence time and volume of approximately 13.8 L. The PAM chamber has several advantages over larger, batch-style smog chambers. First, the PAM chamber is designed with a small volume and short residence time to expedite the atmospheric oxidation process by reacting precursor gases with high levels of oxidants such as OH, O₃, and HO₂. While the mixing ratios of these oxidants are much greater than typical atmospheric levels, the ratios of these oxidants to one another are similar to those ratios found in the atmosphere (Kang et al. 2007). Second, the PAM chamber is designed to minimize interactions with the walls by lowering the surface area to volume ratio. This chamber allows for sampling by multiple devices and for the inclusion of several low-pressure mercury lamps to simulate ultraviolet (UV) radiation from the sun that is essential to initiating photooxidation processes. Studies by Lambe et al. (2011) compare characteristics of SOA
formation in the PAM chamber to formation in other environmental chambers, including the Toronto Photo-Oxidation Tube (TPOT) and Caltech smog chamber. In most cases, the results of all three chambers are comparable. Therefore, the ability of the PAM chamber to simulate atmospheric processes is comparable to larger batch-style smog chambers and even better for some applications. All environmental chambers, however, are disadvantaged by some chemical and physical interactions with the walls of the chambers.

Figure 3.1 depicts a schematic of the experimental setup of the PAM chamber and instruments used to implement the OH counting method, and Figure 3.2 illustrates the PAM chamber and partial laboratory setup as described. Ambient laboratory air is scrubbed by a zero-air generator (Perma Pure LLC) that pushes air through the entire system. The relative humidity (RH) of the air is controlled by a desiccant (Drierite) and a bubbler. The bubbler consists of a sealed glass container that bubbles air through de-ionized water. A bypass and valve around the bubbler allows for the proportion of moist air to be varied to achieve the desired RH in the sample air. Temperature and RH are monitored by a Sensirion USB SHT1x Temperature and Relative Humidity Sensor. The sample air is then combined with predetermined amounts of sulfur dioxide (SO₂), O₃, and a precursor gas, X, that are controlled by calibrated flow controllers (MKS Inc.).

![Figure 3.1 Diagram of experimental setup with the PAM chamber and instrumentation.](image)
The precursor gas is either CO for the creation of the calibration curve or a VOC for comparison and application of the OH counting method. Ozone is added to the air sample by running O$_2$ through an external ozonator that consists of a sealed glass container with a small mercury lamp supplying 185 nm radiation to photolyze O$_2$, producing O atoms that react with O$_2$ to form O$_3$.

This air sample is then mixed thoroughly in the PAM chamber. The mercury lamps in the PAM chamber are controlled by a variable power supply that allows the light intensity in the chamber to be varied by changing the supplied voltage between 0 and 110 volts. The lamps are also encased in Teflon-coated quartz tubing filled by nitrogen (N$_2$) to prevent damage to the lamps from the chemistry occurring in the chamber and the production of O$_3$ within the quartz tubing. This tubing allows 254 nm but restricts 185 nm radiation from initiating photochemistry within the chamber which has been suggested to alter particle chemistry (Kroll et al. 2006; Surratt et al. 2006; Warren et al. 2008). The 254 nm radiation initiates the photolysis of O$_3$ in the PAM chamber that leads to the production of OH radicals via the following reaction mechanisms.

![Figure 3.2 Photograph of the PAM chamber and partial laboratory setup including the SO$_2$ and CO analyzers, UV lamp variable power supply, and flow controllers.](image-url)
The gas mixture is then sampled by appropriate analyzers before being exhausted to a fume hood. An overflow line to the exhaust prevents the buildup of pressure and fluctuations prior to sampling by the gas analyzers. The level of SO$_2$ is monitored by a Thermo Scientific Model 43i-TLE SO$_2$ Analyzer, CO is monitored by a Thermo Scientific Model 48i-TLE CO Analyzer, and O$_3$ is monitored by a Thermo Scientific Model 49i O$_3$ Analyzer. The presence of VOCs in the system is indicated by an SRI Instruments Model 8610C Gas Chromatograph with flame ionization detector (GC-FID). Although this GC-FID has a stated detection limit of 1 ppm, further testing with the VOCs used in these experiments indicate that the presence of the VOCs can be detected down to $\sim$75 ppb.

### 3.2 Experimental Procedure

The OH counting method can be tested with any precursor gas by using the experimental setup described in Section 3.1. Experiments with VOCs are performed over a range of atmospherically relevant mixing ratios, but generally with mixing ratios above those measured in the atmosphere up to approximately 650 ppb. Experiments with the calibration gas, CO, are performed over a range of OH exposures that encompass the range of OH exposures measured for the VOCs. During all experiments, OH exposure is measured in the sample air while maintaining the following conditions: 20 $\pm$ 0.2\% RH, 25 $\pm$ 3°C temperature, 60 $\pm$ 8 ppb SO$_2$, 12.5 $\pm$ 0.2 ppm O$_3$, and 5 L min$^{-1}$ total flow rate, which corresponds to an average residence time of approximately 165 s. Experiments are performed at the relatively low RH of 20\% because concurrent OH exposure experiments indicate that OH exposure is more sensitive to changes in $\Delta$OH with low RH.

An OH exposure curve is constructed by measuring the OH exposure at various mixing ratios of the precursor gas. For every experiment, the OH exposure is measured first for the
chamber in the absence of the precursor gas. This measurement is an indicator of the level of OH produced in the PAM chamber with only zero air, O\textsubscript{3}, and SO\textsubscript{2} added to the system. In all cases, the OH exposure measured for these initial conditions will be the greatest OH exposure measured for the OH exposure curve. When a precursor gas is added to the system, OH radicals are consumed, lowering the measured OH exposure.

The OH exposure for any mixing ratio of a precursor gas is determined by measuring [SO\textsubscript{2}] in the chamber while the UV lamps are turned off and then measuring [SO\textsubscript{2}] again when the UV lamps are turned on. These SO\textsubscript{2} measurements are recorded once the system reaches equilibrium in each state and [SO\textsubscript{2}] is stabilized which takes approximately 10 to 15 minutes for the experimental conditions described. When the UV lamps are on, a certain amount of SO\textsubscript{2}, as well as the precursor gas if present, is consumed by the OH radical. When the mixing ratio of the precursor gas is varied, the amount of SO\textsubscript{2} consumed by the OH radical will vary as well because the precursor gas is competing with SO\textsubscript{2} for consumption of the OH radical. In this way, SO\textsubscript{2} is used to monitor the level of OH radicals in the PAM chamber. The definition of OH exposure is solved analytically to calculate the value of OH exposure as a function of this SO\textsubscript{2} decay (Kang et al. 2011) as follows:

\[
OH \text{ exposure} = \frac{1}{k_{SO_2+OH}} \ln \left( \frac{(SO_2)_i}{(SO_2)_f} \right) \quad (5)
\]

where \( k_{SO_2+OH} \) is the second-order reaction rate coefficient for SO\textsubscript{2} + OH, \((SO_2)_i\) is the initial mixing ratio of SO\textsubscript{2} when the UV lamps are turned off, and \((SO_2)_f\) is the final mixing ratio of SO\textsubscript{2} with the UV lamps turned on.

The same procedure is used to measure OH exposure for both the calibration gas, CO, and each VOC. At each VOC mixing ratio, the entire amount of the added VOC (\(\Delta\)VOC) is assumed to be reacted away when the lamps are turned on in the PAM chamber. The GC-FID is implemented to verify this assumption by indicating if any amount of the VOC is left in the PAM.
chamber after the system has reached equilibrium. The GC-FID, however, has a detection limit of ~75 ppb; therefore, a simple model of PAM chamber chemistry is also used to indicate if significant amounts of the added VOC remain in the chamber once the system has reached equilibrium. This model is described in more detail in Chapter 5. If the entire amount of the VOC added is reacted away with the OH radical, then the amount of the VOC added is a measure of how many OH radicals are consumed in the initial reaction with that VOC. From this, the OH exposure curve for the VOC can be constructed by plotting ΔVOC, which is equal to ΔOH, as a function of OH exposure, according to the theory described in Section 2.2.

On the other hand, not all of the added calibration gas will be consumed in the PAM chamber because CO reacts more slowly with the OH radical than do the VOCs. Therefore, [CO] is measured by the CO analyzer when the lamps are turned off and again when the lamps are turned on. The difference between these values is a measure of the number of OH radicals consumed by CO so that the calibration curve is constructed by plotting ΔCO, which is equal to ΔOH, as a function of OH exposure.

The experiments outlined in Table 3.1 are implemented to test the OH counting method and explore characteristics of the OH exposure curves using these experimental and analysis procedures. Other ambient conditions, including RH, temperature, flow rate, and SO₂ and O₃ mixing ratios, are constant for all experiments. The four different initial OH exposures outlined in Table 3.1 are achieved by varying the voltage supplied to each of the UV lamps, thus changing the light intensity and amount of OH radicals produced in the chamber. All experiments outlined are conducted with two UV lamps though the PAM chamber is setup for experimentation with up to four lamps. Voltage can be varied between 0 and 110 volts with the variable power supply. Different combinations of voltages on each lamp can produce the same OH exposures; therefore, voltages are indicated in estimated ranges based on the lamp settings used in the OH exposure experiments.
**Table 3.1** Summary of the VOC and CO OH exposure experiments performed to test the OH counting method. The voltage range is the estimated voltage settings for each UV lamp used to obtain each light intensity and associated initial OH exposure for experiments. The modeled actinic flux is an estimate of the flux in the chamber using a simple PAM chamber chemistry model.

<table>
<thead>
<tr>
<th>Initial OH Exposure (molecules cm$^{-3}$ s$^{-1}$)</th>
<th>Voltage Range (volts)</th>
<th>Modeled Actinic Flux (photons cm$^{-3}$ s$^{-1}$)</th>
<th>Precursor Gas</th>
<th>Precursor Gas Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>~5.0 x 10$^{11}$</td>
<td>61 – 78</td>
<td>2.30 x 10$^{14}$</td>
<td>α-pinene</td>
<td>0 – 650 ppb</td>
</tr>
<tr>
<td>~8.7 x 10$^{11}$</td>
<td>64 – 89</td>
<td>5.05 x 10$^{14}$</td>
<td>CO, propane, isoprene, m-xylene, α-pinene</td>
<td>0 – 30 ppm, 0 – 650 ppb, 0 – 650 ppb</td>
</tr>
<tr>
<td>~13.2 x 10$^{11}$</td>
<td>90 – 110</td>
<td>8.93 x 10$^{14}$</td>
<td>α-pinene</td>
<td>0 – 650 ppb</td>
</tr>
<tr>
<td>~18.9 x 10$^{11}$</td>
<td>99 – 110</td>
<td>1.43 x 10$^{15}$</td>
<td>CO, propane, isoprene, m-xylene, α-pinene</td>
<td>0 – 30 ppm, 0 – 650 ppb, 0 – 650 ppb</td>
</tr>
</tbody>
</table>

For all OH exposure experiments, the reproducibility of results is verified; this data, however, is not included in the datasets here. All gas measurements are recorded as mixing ratios in parts per billion (ppb) or parts per million (ppm). These mixing ratios are then converted to an OH radical concentration (molecules cm$^{-3}$) by multiplying the mixing ratio by a calculated number of air molecules (M). The number of air molecules is determined from ambient temperature and pressure, assuming that the pressure in the PAM chamber is 2% below atmospheric pressure.

**3.3 SO$_2$ as a Monitoring Gas**

The OH counting method uses SO$_2$ as a means to monitor the level of OH radicals in the PAM chamber. The use of SO$_2$ as a monitoring gas has been extensively tested in other PAM
chamber studies and proven to be a useful metric for indicating the level of OH radicals present (Kang et al. 2011; Lambe et al. 2012). This theory assumes that all SO₂ consumed is oxidized by the OH radical with a reaction rate coefficient of $9.5 \times 10^{-13}$ cm³ molecules⁻¹ s⁻¹. Although SO₂ is also consumed by other oxidants, the reaction rates are negligibly slow. The reaction rate coefficient at 298 K for the reaction between SO₂ and O₃ is $< 2 \times 10^{-22}$ cm³ molecules⁻¹ s⁻¹ and for the reaction between SO₂ and HO₂ is $< 1 \times 10^{-18}$ cm³ molecules⁻¹ s⁻¹ (NASA JPL Eval. No. 17, 2011). The dominant reactions in the PAM chamber proceeding from the oxidation of SO₂ by the OH radical are outlined in (R17) through (R20).

\[ SO_2 + OH + M \rightarrow HOSO_2 + M \]  \hspace{1cm} (R17)
\[ HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \]  \hspace{1cm} (R18)
\[ SO_3 + H_2O + M \rightarrow H_2SO_4 + M \]  \hspace{1cm} (R19)
\[ H_2SO_4 + H_2O \rightarrow sulfate \ aerosol \]  \hspace{1cm} (R20)

Sulfur dioxide is useful as a monitoring gas for the OH counting method for several of the same reasons CO is ideal as a calibration gas.

1. One SO₂ molecule is consumed for each OH radical consumed in the reaction; therefore, SO₂ can be used to monitor the amount of OH present in the PAM chamber at any given time.

2. The OH radical is the primary removal mechanism for SO₂ in the atmosphere; therefore, this is also the case for the PAM chamber.

3. The products in (R17) through (R20) are not likely to consume or produce additional OH radicals which would alter the measurement of OH exposure. This assertion, however, is complicated by the production of HO₂ in (R18) which can lead to regeneration of the OH radical. Because of the amount of SO₂ added to the system is small, any regeneration of the OH radical from HO₂ is assumed negligible.
(4) Accessible and accurate monitoring devices exist for the measurement of SO₂.

(5) The amount of SO₂ necessary for the use as a monitoring gas is small enough that any chemistry initiated by the presence of SO₂ has negligible effects on the overall level of OH radicals and on the VOC chemistry in the PAM chamber.

3.4 Gas Mixtures

All VOC gas mixtures are prepared in house in the Pennsylvania State University laboratory facilities by injecting the VOC mixture into an evacuated 3L metal canister (Restek SilcoCan). All metal canisters are cleaned by a repeated process of heating and purging with N₂ before each new mixture is prepared. Nitrogen is also used as the balance gas to increase the pressure and create a mixture of ~150 ppm in the canister. The general procedure for creating these VOC gas mixtures is outlined in more detail in Kang et al. (2007). Isoprene, α-pinene, and m-xylene are added to the canisters using a syringe injection method. The stated purities of these VOC sources are isoprene (99%, Sigma-Aldrich), α-pinene (>99%, Sigma-Aldrich), and m-xylene (99.5%, Fluka). Propane mixtures are prepared by introducing highly concentrated gas from a lecture bottle (99.97%, Tri-Matheson Gas).

All other gas mixtures necessary for experimentation are standard or custom-ordered gas mixtures with the following purities and sources: O₂ (99.994%, Praxair), SO₂ (>99%, Scott Marrin), N₂ (99.999%, Praxair), and CO (98%, Scott Marrin). Hydrogen (H₂) is also used in the operation of the GC-FID with a purity of >99% (GT&S Inc.).
Chapter 4
RESULTS AND DISCUSSION

Using the theory and methods outlined in Chapters 2 and 3, experiments are carried out to implement the OH counting method by constructing OH exposure curves for CO and for the atmospherically relevant VOCs, propane, isoprene, m-xylene, and α-pinene. These results reveal unique characteristics about the oxidation reactions between these VOCs and the OH radical. Sources of error and uncertainties introduced in the laboratory techniques while implementing the OH counting method are also discussed in this chapter.

4.1 Laboratory Results

The results of the experiments exploring the OH counting method are presented first by the raw OH exposure data and construction of the OH exposure curves for the four atmospheric VOCs and calibration gas, CO. Then, these curves are compared to determine the number of OH radicals consumed per initial VOC molecule oxidized.

VOC OH Exposure Curves

The number of OH radicals produced in the PAM chamber is highly dependent on the light intensity of the UV lamps. The actual actinic flux in the PAM chamber, however, is not applicable to the atmosphere. This dependence is illustrated in Figure 4.1 which displays OH exposure curves constructed for α-pinene oxidation in four experiments at different light intensities. Recall that ΔOH is the amount of α-pinene added to the system, assuming that all α-pinene is reacted away with the OH radical once the system has reached equilibrium with the UV
lamps turned on. In all four α-pinene experiments, measurements by the GC-FID verify this assumption to the detection limit of the instrument. The best-fit lines (black) in Figure 4.1 are constructed by second-order polynomials to fit the OH exposure data, and all have a coefficient of determination ($R^2$) value > 0.99. For the case of $\Delta \text{OH} = 0$ molecules cm$^{-3}$, the OH exposure measured at each light intensity is representative of the initial conditions in the chamber in the absence of the VOC. Therefore, there is a direct correlation between light intensity and OH exposure. The UV lamps supply 254 nm radiation that photolyzes O$_3$ in the presence of water vapor to produce the OH radical; therefore, a greater light intensity leads to the production of more OH radicals and a higher OH exposure in the PAM chamber.

A negative correlation exists between $\Delta \text{OH}$ and OH exposure. At each light intensity, $\Delta \text{OH}$ increases when known amounts of α-pinene are added to the system, and the OH exposure

![Figure 4.1](圖像)

**Figure 4.1** OH exposure curves constructed by α-pinene oxidation at four different light intensities. Data with the highest OH exposures (red square) is obtained with the highest light intensity, and data with the lowest OH exposures (purple circle) is obtained with the lowest light intensity. Solid black lines are second-order polynomials fitted to the data with $R^2 > 0.99$. 
decreases because more OH radicals are consumed by this VOC and its oxidation products, lowering the level of OH radicals in the PAM chamber. The OH exposure curves are, however, more sensitive to changes in the amount of the VOC added as the light intensity increases. The OH exposures in Figure 4.1 are also influenced by the ozonolysis of α-pinene. At the highest light intensity, the greatest number of OH radicals are produced because the greatest number of O₃ molecules are photolyzed. Therefore, the ozonolysis of α-pinene has the least impact on the OH exposure curve with the highest light intensity and the greatest impact on the curve with the lowest light intensity. According to simple modeling efforts, about 4% of ΔOH for the highest light intensity is attributable to ozonolysis and over 10% for the lowest light intensity. The effect of ozonolysis on the application of the OH counting method is discussed further in Section 4.2.

The OH counting method is tested at two of the light intensities in Figure 4.1. Figure 4.2 displays the OH exposure curves for CO, propane, isoprene, and m-xylene at these two light intensities for comparison. These curves exhibit many of the same light-dependent characteristics as the α-pinene OH exposure curves in Figure 4.1. All VOCs are added to the chamber up to a mixing ratio of approximately 650 ppb. Carbon monoxide, on the other hand, is added to achieve the appropriate range of OH exposures which equates to approximately 30 ppm of CO for both the higher and lower light intensity experiments in Figure 4.2(a).

Figure 4.3 displays the OH exposure curves for these four VOCs and CO at the higher light intensity with an initial OH exposure of ~18.9 x 10¹¹ molecules cm⁻³ s. The ΔOH values estimated by the calibration curve are a factor of two or greater than the ΔOH for the VOC OH exposure curves. According to the OH counting method, this indicates that the VOC oxidation products are, overall, consuming additional OH radicals after the initial OH radical attack. Of these VOCs, m-xylene and its oxidation products consume the most OH radicals, evidenced in Figure 4.3 by the lowest measured OH exposures for an equivalent amount of VOC added. Low OH exposures indicate that a high level of OH radicals have been depleted by the VOC and subsequent oxidation products. After m-xylene and its oxidation products, the most OH radicals
are consumed by isoprene, $\alpha$-pinene, and finally propane and the respective oxidation products of each.

Figure 4.4 displays the OH exposure curves for these four atmospheric VOCs and CO at a lower light intensity with an initial OH exposure of $\sim 8.7 \times 10^{11}$ molecules cm$^{-3}$ s. The interpretation of these OH exposure curves at the lower light intensity is much the same as at the higher light intensity though striking differences in the data exist. Common to OH exposure curves at both light intensities is the order of the VOCs in terms of OH radical consumption; $m$-xylene and its reaction products consume the most OH radicals, followed by isoprene, $\alpha$-pinene, and propane and their respective oxidation products. For the lower light intensity, however, this is

Figure 4.2 OH exposure curves constructed for (a) CO, (b) propane, (c) isoprene, and (d) $m$-xylene oxidation at an initial OH exposure of $\sim 18.9 \times 10^{11}$ molecules cm$^{-3}$ s. Solid black lines are second-order polynomials fitted to the data with $R^2 > 0.993$ to guide the eye.
only true for the highest $\Delta OH$ values.

Contrary to the higher light intensity, $\Delta OH$ for CO at the lower light intensity is greater than the $\Delta OH$ for the VOC OH exposure curves by a factor of four or less for all VOCs and less than two for propane, specifically. In general, these VOCs and their oxidation products are consuming fewer OH radicals at the lower light intensity than at the higher light intensity which indicates the dependence of these results on the initial conditions chosen for each experiment. Furthermore, the shape of the OH exposure curves for these VOCs exhibit unique characteristics compared to those at the higher light intensity. In Figure 4.4, at the lower light intensity, the OH exposure curves for isoprene and $\alpha$-pinene have a noticeably different curvature compared to those of propane and $m$-xylene; this difference, however, is not distinct at the higher light intensity. A depiction of the OH exposure curves for the VOCs only is located in Appendix A.
The curvature of an OH exposure curve is affected by numerous factors related to and specific to the different VOC oxidation mechanisms. For instance, the ozonolysis of a VOC is likely to change the curvature of an OH exposure curve. When VOC molecules are consumed by O$_3$, rather than the OH radical, there are a greater number of OH radicals remaining in the system for other interactions, effectively changing the relationship between ∆OH and OH exposure. Additionally, as the amount of the VOC added to the system increases, this effect becomes greater, causing the OH exposure measured to be higher than expected for VOC consumption by the OH radical alone. Ozonolysis also changes the profile of oxidation products in the PAM chamber. As discussed, isoprene and α-pinene are both reactive with O$_3$, whereas propane and m-xylene react too slowly to be considered. At the lower light intensity, the influence of O$_3$ on the OH exposure curves is greater because fewer O$_3$ molecules are photolyzed and fewer OH radicals

![Figure 4.4](image-url) OH exposure curves constructed for CO, propane, isoprene, m-xylene, and α-pinene oxidation at an initial OH exposure of ~8.7 x 10$^{11}$ molecules cm$^{-3}$ s. Solid black lines are second-order polynomials fitted to the data with $R^2 > 0.993$ to guide the eye.

The curvature of an OH exposure curve is affected by numerous factors related to and specific to the different VOC oxidation mechanisms. For instance, the ozonolysis of a VOC is likely to change the curvature of an OH exposure curve. When VOC molecules are consumed by O$_3$, rather than the OH radical, there are a greater number of OH radicals remaining in the system for other interactions, effectively changing the relationship between ∆OH and OH exposure. Additionally, as the amount of the VOC added to the system increases, this effect becomes greater, causing the OH exposure measured to be higher than expected for VOC consumption by the OH radical alone. Ozonolysis also changes the profile of oxidation products in the PAM chamber. As discussed, isoprene and α-pinene are both reactive with O$_3$, whereas propane and m-xylene react too slowly to be considered. At the lower light intensity, the influence of O$_3$ on the OH exposure curves is greater because fewer O$_3$ molecules are photolyzed and fewer OH radicals
are produced as competition for the ozonolysis of these VOCs. Therefore, this effect is more likely to be observed for the lower light intensity than the higher light intensity.

Another possible explanation for the variation in curvature between VOC OH exposure curves is the difference in the effective residence time in the PAM chamber for each VOC. When a certain amount of VOC is added to the PAM chamber, the concentration of OH radicals initially decreases rapidly because of VOC and oxidation product consumption but eventually comes to a steady state concentration. The time-dependent profile of the OH radical concentration in the PAM chamber is likely to vary by VOC because of the unique combination of oxidation products each VOC produces, thus changing the effective residence time for each VOC. Varying effective residence times for each VOC can change the relationship between ΔOH and OH exposure.

Finally, the difference in reaction rate coefficients between the OH radical and each of these VOCs can alter the curvature of the OH exposure curves. The simple PAM chamber chemistry model, however, indicates that this reaction characteristic does not change curves by the magnitude or in the way necessary to explain the unique curvature of the isoprene and α-pinene OH exposure curves. This model does, however, suggest that the ozonolysis of these VOCs can affect the curves in a similar manner observed in the OH exposure data. These modeling efforts are discussed further in Chapter 5.

**Consistency of the Experimental Conditions**

The numerous analyzers described in Chapter 3 are used to ensure that conditions remain constant between and during each experiment constructing OH exposure curves. Another useful metric for maintaining stable conditions from one experiment to the next is the amount of O₃ lost in the PAM chamber during the measurement of OH exposure, or ΔO₃. The ΔO₃ is the difference between the [O₃] measured when the system is at equilibrium with the UV lamps off and the [O₃] measured again with the UV lamps on. When the UV lamps are off, the stable O₃ concentration is maintained at approximately 12.5 ppm for all OH exposure experiments. When the UV lamps are
turned on, O$_3$ is photolyzed by 254 nm radiation in the PAM chamber to produce OH radicals, thus decreasing the O$_3$ concentration in the system. In this way, $\Delta$O$_3$ is also an indicator of the number of OH radicals produced in the PAM chamber for a given set of conditions. Figure 4.5 illustrates this concept with the four $\alpha$-pinene experiments performed at different light intensities. The $\Delta$O$_3$ measured for the initial OH exposure, or for the $\Delta$OH = 0 molecules cm$^{-3}$ case, is indicated by the black circles in Figure 4.5. As expected, as light intensity and initial OH exposure decrease, $\Delta$O$_3$ also decreases because fewer O$_3$ molecules are photolyzed and then react with water (H$_2$O) to form OH radicals. This measurement, however, has no practical applicability to the atmosphere and is only useful as a metric to ensure the consistency of experimental conditions.

![Figure 4.5](image_url)

*Figure 4.5* The metric $\Delta$O$_3$ plotted as a function of OH exposure for the four different light intensity experiments for $\alpha$-pinene, as indicated by symbols. Data with the highest OH exposures (red square) is obtained with the highest light intensity, and data with the lowest OH exposures (purple circle) is obtained with the lowest light intensity. The $\Delta$O$_3$ values for the initial OH exposure, or the $\Delta$OH = 0 molecules cm$^{-3}$ case, are indicated by the black circles.
For each experiment at the same light intensity, the ΔO₃ measured for the initial OH exposure should be the same assuming that all conditions in the PAM chamber are consistent between experiments. Figure 4.6 illustrates the ΔO₃ measurement as a function of OH exposure for the addition of different amounts of CO, propane, isoprene, m-xylene, and α-pinene for both light intensities used to test the OH counting method. The initial ΔO₃ measurements at each light intensity, OH exposure ≈ 18.9 x 10¹¹ molecules cm⁻³ s for the higher light intensity and OH exposure ≈ 8.7 x 10¹¹ molecules cm⁻³ s for the lower light intensity, agree to within the level of uncertainty estimated in the laboratory experiments. Therefore, experimental conditions were kept reasonably constant for all OH exposure experiments. The uncertainty in ΔO₃ is approximately ± 10% for the higher light intensity and ± 20% for the lower light intensity.

Almost all ΔO₃ measurements have a positive trend with OH exposure, m-xylene being an exception. In the PAM chamber, the ΔO₃ is due primarily to photolysis and consumption by the OH and HO₂ radicals. Figure 4.7 illustrates the contributions of these three sinks to O₃ consumption in the PAM chamber for the case of CO at the highest light intensity as estimated by the simple PAM chamber chemistry model. This model predicts approximately 40% O₃ consumption by photolysis, 50% by the OH radical, and 10% by the HO₂ radical at an initial OH exposure of ~18.9 x 10¹¹ molecules cm⁻³ s. The ΔO₃ consumed by photolysis does not vary with OH exposure; therefore, the general trend of ΔO₃ is due to the reactions between the OH and HO₂ radicals with O₃, the kinetics of which proceed at a rate slower than the VOCs and CO with the OH radical. As the amount of VOC added to the system increases, the OH exposure decreases, and more OH radicals are consumed by the VOC and its oxidation products, leaving fewer OH radicals for consumption by O₃. Therefore, as OH exposure decreases, fewer O₃ molecules are consumed by the OH radical, leading to lower ΔO₃ values.

The slope of the ΔO₃ data, however, varies by VOC. While the general positive trend is most significantly determined by the OH and HO₂ reactions with O₃ as described, several other factors can vary the slope of ΔO₃ for each VOC. For instance, because each VOC produces a
Figure 4.6 The metric $\Delta O_3$ plotted as a function of OH exposure for the (a) higher light intensity and (b) lower light intensity. This metric ensures experimental conditions remain constant for the construction of each OH exposure curve for the four atmospheric VOCs and CO.
unique combination and yield of oxidation products, any O₃ interactions with those products is likely to alter the slope of the ΔO₃ data in a distinct way. Furthermore, the ΔO₃ measurements are raw data from OH exposure experiments and are not adjusted for reaction with any of the VOCs tested. Therefore, measurements of ΔO₃ for the isoprene and α-pinene experiments are skewed because the initial O₃ measurement is reduced by O₃ reactions with these VOCs. These reactions also lead to decreasing ΔO₃ values as OH exposure decreases, effectively steepening the slope of the ΔO₃ data. In general, because the slope of ΔO₃ is dependent on O₃ reactions with the OH and HO₂ radicals, any interactions of VOC oxidation products with O₃ or the HOₓ radicals can also impact the slope of ΔO₃.

![Figure 4.7](image-url)

**Figure 4.7** Modeled ΔO₃ plotted as a function of OH exposure for the case of CO at the highest light intensity with different contributions to O₃ consumption in the PAM chamber.
Counting OH Radicals

The OH counting method is tested on propane, isoprene, m-xylene, and α-pinene using the OH exposure curves displayed in Figures 4.3 and 4.4. These OH exposure curves are used to obtain the number of OH radicals consumed by a VOC and its OH-initiated oxidation products per VOC molecule oxidized. The number of OH radicals consumed per VOC molecule oxidized is determined by dividing the ∆OH values on the calibration curve (ΔCO) by the values on each VOC OH exposure curve (ΔVOC) at corresponding OH exposures. Figures 4.8 and 4.9 demonstrate the application of the OH counting method and use of the described analysis technique in estimating the number of OH radicals consumed per VOC molecule oxidized (ΔCO/ΔVOC) for the higher and lower light intensity experiments, respectively. These ΔCO/ΔVOC curves are constructed from data represented by second-order polynomial fits with $R^2 > 0.993$ for all cases. Higher-order polynomial fits are also explored, but higher-order fits did not significantly change the ΔCO/ΔVOC curves for many cases. Moreover, for certain cases, however, higher-order polynomials introduce uncharacteristic oscillatory effects in the OH exposure curves and were therefore disregarded.

Recall that the calibration curve represents the actual number of OH radicals consumed in the PAM chamber at any OH exposure and assumes that ΔCO is equal to ∆OH. The VOC OH exposure curves represent the OH exposure for all reactions between the OH radical and the VOC and subsequent reaction products, and ΔVOC is the number of VOC molecules oxidized and equal to ∆OH from initial reactions alone. Therefore, dividing ΔCO by ΔVOC at any given OH exposure yields the net number of OH radicals consumed per VOC molecule oxidized. It is appropriate to compare values at the same OH exposure because OH exposure is an indicator of the level of OH radicals in the chamber; therefore, ΔCO and ΔVOC are compared when the same conditions are present in the PAM chamber as indicated by OH exposure.
The $\Delta CO/\Delta VOC$ values for the higher and lower light intensity experiments are not calculated over a range of OH exposures near the initial OH exposure. The $\Delta CO/\Delta VOC$ values are not calculated at OH exposures greater than ~$17.5 \times 10^{11}$ molecules cm$^{-3}$ s for the higher light intensity in Figure 4.8 and greater than ~$7.75 \times 10^{11}$ molecules cm$^{-3}$ s for the lower light intensity in Figure 4.9. The OH exposure cutoff for each light intensity is based on uncertainties estimated by the respective OH exposure curves in Figures 4.3 and 4.4. This data is disregarded because the level of uncertainty is too great to draw useful conclusions. The uncertainties in $\Delta CO/\Delta VOC$ in these ranges are exacerbated by the small $\Delta CO$ and $\Delta VOC$ values and misalignment of initial OH exposures in the OH exposure curves in Figures 4.3 and 4.4. Furthermore, because each

![Figure 4.8](image)

**Figure 4.8** The number of OH radicals consumed per VOC molecule oxidized as a function of OH exposure at the higher light intensity tested. Curves are constructed by dividing $\Delta CO$ values on the calibration curve by $\Delta VOC$ values from the VOC OH exposure curves at each value of OH exposure. Solid lines are $\Delta CO/\Delta VOC$ curves constructed by OH exposure data that is represented by a second-order polynomial fit ($R^2 > 0.995$ for all OH exposure curves). Uncertainties for the $\Delta CO/\Delta VOC$ curves are indicated by the shaded regions.
\( \Delta \text{CO}/\Delta \text{VOC} \) curve relies on the representative polynomial fit, uncharacteristic \( \Delta \text{CO}/\Delta \text{VOC} \) values are determined when OH exposure curves intersect or become negative in these regions. Additionally, there is too little data in this region to reasonably characterize the unique behavior that is observed in this small range of OH exposures. For all of these reasons, \( \Delta \text{CO}/\Delta \text{VOC} \) values in these ranges of OH exposure are omitted. Unfortunately, neglecting these data also omits a part of the range of OH exposures that represent the most atmospherically relevant VOC mixing ratios.

The \( \Delta \text{CO}/\Delta \text{VOC} \) values for the higher light intensity are approximately a factor of two greater than those values for the lower light intensity. This difference may be caused by the OH

![Figure 4.9](image_url)

**Figure 4.9** The number of OH radicals consumed per VOC molecule oxidized as a function of OH exposure at the lower light intensity tested. Curves are constructed by dividing \( \Delta \text{CO} \) values on the calibration curve by \( \Delta \text{VOC} \) values from the VOC OH exposure curves at each value of OH exposure. Solid lines are \( \Delta \text{CO}/\Delta \text{VOC} \) curves constructed by OH exposure data that is represented by a second-order polynomial fit (\( R^2 > 0.993 \) for all OH exposure curves). Uncertainties for the \( \Delta \text{CO}/\Delta \text{VOC} \) curves are indicated by the shaded regions.
reactivity created by each set of experimental conditions and possible increased light effects in the higher light intensity experiments. The amount of VOC added to the chamber has the most significant impact on OH exposure; therefore, at higher OH exposures, when smaller amounts of VOC are in the chamber, a relatively smaller fraction of OH radicals is consumed by the initial VOC, allowing more OH radicals to interact with oxidation products and participate in aerosol aging processes. At lower OH exposures, when greater amounts of VOC are added, a greater fraction of OH radicals is consumed by the initial VOC, leaving less OH radicals remaining to interact with the oxidation products and aerosol. Therefore, these processes make it probable that more OH radicals are consumed per VOC molecule oxidized in the higher light intensity experiments and in the presence of more OH radicals.

In general, ΔCO/ΔVOC decreases as OH exposure decreases. This general trend may be explained by the same reason that ΔCO/ΔVOC values are higher for the higher light intensity experiments. Aerosol aging processes, however, may also play an increasingly important role. When higher levels of VOCs are present in the PAM chamber, more particles are created by the oxidation products. More particles make an increasing amount of mass less accessible to the OH radical for oxidation reactions. This would indicate a tendency for fewer OH radicals to be consumed per VOC molecule oxidized as the initial amount of VOC added to the chamber increases. This idea is consistent with the results of Kang et al. (2011) that find that aerosol become increasingly less oxidized as mass concentration of organic aerosol increases. Therefore, ΔCO/ΔVOC tends to decrease as OH exposure decreases. While simple modeling efforts agree with this trend, more sophisticated modeling may be necessary to determine the importance of the gas and aerosol-phase chemistry.

All of the OH exposure curves constructed, regardless of polynomial fit and light intensity, have a maximum in ΔCO/ΔVOC near the higher range of experimental OH exposures. The magnitude of the maximum, however, may yield no useful information because there is too much uncertainty, as described, in ΔCO/ΔVOC at the highest OH exposures of each experiment.
Moreover, some maximums are artifacts of the best-fit polynomial curves used to fit the data and likely have no significance.

Similar to the OH exposure data for the lower light intensity in Figure 4.4, the ∆CO/∆VOC curves for isoprene and α-pinene exhibit a unique shape from the other VOCs. This effect stems from the same unique curvature apparent in the OH exposure data for these VOCs. Therefore, these local maxima in the mid-range OH exposures of the ∆CO/∆VOC curves are likely due to the effects caused by the ozonolysis of these VOCs or differences in effective residence time.

4.2 Sources of Error and Uncertainty

This section outlines the sources of error and uncertainties introduced while using the OH counting method. The measurement of OH exposure curves in Section 4.1 is subject to effects in the PAM chamber such as wall interactions as well as instrument limitations. The OH counting method is also complicated by the chemistry from VOC ozonolysis, atmospheric photolysis, and reaction kinetics, all of which are discussed here.

Wall Interactions

All environmental chambers are limited in their likeness to the atmosphere by walls. The PAM chamber is designed to minimize interactions with the walls of the chamber, though this problem cannot be completely mitigated. Some interactions with the walls of the PAM chamber are observed during experimentation. For instance, the concentration of SO₂ in the chamber decreases as RH increases. This can be attributed to the solubility of SO₂ in H₂O, the product of which sticks to the walls of the chamber. It is also likely that some of the lower volatility products and particles formed from VOC oxidation stick to the walls of the PAM chamber. These effects, however, are assumed negligible in the application of the OH counting method because the OH wall loss is a constant loss frequency and does not depend on the type or amount of the VOC.
VOC Ozonolysis

The OH counting method relies on the OH radical as the dominant loss mechanism for all of the VOCs tested. Making this assumption allows ∆VOC to be equal to ∆OH from initial reactions alone. Ozone, however, can compete for consumption of certain VOCs, such as isoprene and α-pinene. Thus, ∆VOC cannot be entirely attributed to OH radical consumption. Table 4.1 provides estimates of the fraction of ∆VOC consumed by O₃ rather than the OH radical based on the calculation of the frequency of OH radical and O₃ reactions in the PAM chamber. Propane and m-xylene react slowly enough with O₃ that any effects to ∆OH are negligible; significant amounts of isoprene and α-pinene, however, are consumed by O₃ rather than the OH radical. Less than 1% of isoprene consumption is by O₃ whereas up to 9% of α-pinene consumption is by O₃. The VOC ozonolysis is greater for the lower light intensity experiments because relatively fewer OH radicals are produced, allowing for greater competition by O₃. Although O₃-initiated oxidation mechanisms lead to a different product yield than OH-initiated

Table 4.1 Estimation of the fraction of ∆VOC consumed by O₃ rather than the OH radical in the application of the OH counting method. The mixing ratio of the OH radical, [OH], is estimated from the simple PAM chamber model, assuming an average value over the residence time. The mixing ratio of O₃, [O₃], is conservatively assumed to be 12.5 ppm, the initial mixing ratio of O₃ in the system during each experiment.

<table>
<thead>
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<th>VOC</th>
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<th>Low Light Intensity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kₒ₉[OH] (s⁻¹)</td>
<td>kₒ₃[O₃] (s⁻¹)</td>
<td>O₃ consumption (%)</td>
<td>kₒ₉[OH] (s⁻¹)</td>
</tr>
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<td>propane</td>
<td>1.3 x 10⁻³</td>
<td>2.0 x 10⁻¹⁰</td>
<td>&lt;&lt; 0.01</td>
<td>6.1 x 10⁻⁴</td>
</tr>
<tr>
<td>isoprene</td>
<td>1.2 x 10⁻¹</td>
<td>3.9 x 10⁻⁴</td>
<td>0.3</td>
<td>5.6 x 10⁻²</td>
</tr>
<tr>
<td>m-xylene</td>
<td>2.8 x 10⁻²</td>
<td>7.2 x 10⁻⁸</td>
<td>&lt; 0.01</td>
<td>1.3 x 10⁻²</td>
</tr>
<tr>
<td>α-pinene</td>
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<td>2.7 x 10⁻³</td>
<td>4</td>
<td>3.0 x 10⁻²</td>
</tr>
</tbody>
</table>
oxidation, the composition of the products from OH and O₃-initiated oxidation are similar. Therefore, the ozonolysis of isoprene and α-pinene has little effect on the use of the OH counting method. Theoretical estimates of OH counting taking ozonolysis into account are discussed further in Section 4.3.

**Differences in Reaction Rate Coefficients**

The use of the OH counting method is also dependent on the reaction rate coefficient between the OH radical and the precursor gas. Figure 4.10 depicts the impact of the precursor gas rate coefficient with the OH radical on the construction of OH exposure curves using the simple PAM chamber model. For this exercise, only the initial reaction between the precursor gas and the OH radical are taken into account. Increasing the precursor gas rate coefficient with the OH radical tends to shift the OH exposure curve to the left, decreasing both ΔOH and OH exposure. The spectrum of OH exposure curves ranges from the slowest reacting species with the OH radical, CO and propane, followed by m-xylene and α-pinene, to the fastest reacting with the OH radical, isoprene. Although propane’s reaction rate coefficient with the OH radical is an order of magnitude faster than that of CO with the OH radical, the OH exposure curves for these two precursor gases are almost identical.

The estimated changes in the OH exposure curves due to the reaction rate coefficients between the precursor gases and the OH radical in Figure 4.10 are used in the estimates of uncertainty for the ΔCO/ΔVOC curves in Figures 4.8 and 4.9. For the higher light intensity, isoprene ΔVOC differs from the calibration curve by up to approximately 6%, α-pinene by 5%, m-xylene by 4%, and propane by less than 1%. For the lower light intensity, isoprene ΔVOC differs from the calibration curve by up to approximately 12%, α-pinene by 10%, m-xylene by 6%, and propane by less than 1%. Because varying the reaction rate coefficient from the rate coefficient used to construct the calibration curve has the effect of decreasing ΔOH at any OH exposure, this phenomenon causes greater positive uncertainties in ΔCO/ΔVOC.
OH Recycling in the Calibration Curve

The calibration curve constructed with CO indicates how many OH radicals are consumed in the PAM chamber as a function of OH exposure. The production of HO₂ from the OH-initiated oxidation of CO, however, does lead to the production and consumption of additional OH radicals through various HOₓ mechanisms and alters the OH exposure and OH counting associated with the calibration curve. Figure 4.10 also demonstrates the impact of OH recycling on the calibration curve by allowing or removing HO₂ production using the simple PAM chamber model. For both the lower and higher light intensity cases, removing the HO₂ production from CO oxidation has the effect of changing the curvature of the OH exposure curve. The calibration curves allowing and removing HO₂ production intersect near 5 x 10¹¹ molecules cm⁻³ s⁻¹ for both light intensities.

While OH recycling in the calibration curve can potentially cause significant errors in the calculation of ∆CO/∆VOC, no estimate of an OH recycling error in ∆CO is included in the estimated uncertainties in Figures 4.8 and 4.9. Based on the modeled OH exposure curves, OH recycling can cause ∆OH to decrease by a factor of approximately 0.8 for the higher light intensity and increase by a factor of up to approximately 1.3 for the lower light intensity over the applicable ranges of OH exposures. This difference leads to an approximate increase in ∆CO/∆VOC by a factor of 1.1 to 1.4 for the higher light intensity. For the lower light intensity, this difference leads to an increase in ∆CO/∆VOC of up to a factor of 1.2 at the higher OH exposures and decrease by a factor of 0.85 for the lower OH exposures over the applicable range of OH exposures. It is unlikely, however, that the production of HO₂ in the calibration curve actually generates this much error in the calculation of ∆CO/∆VOC for each of these VOCs. In all of these VOC OH-initiated oxidation mechanisms, similar HO₂ production mechanisms and OH recycling occurs, although the amount and yield per VOC oxidized is likely to vary. Therefore, these estimates of uncertainty due to HO₂ production and OH recycling in the calibration curve serve to put an upper limit on the degree to which the OH counting method may be affected by
Figure 4.10 Modeled OH exposure curves for CO and four VOCs, assuming only the initial OH attack on the precursor gas and no other OH radical interactions with products, for the (a) higher light intensity and (b) lower light intensity experiments. The curves for CO (with HO$_2$ production) and CO (without HO$_2$ production) present the difference in the OH exposure curves from the recycling of the OH radical from the reactions, CO + OH $\rightarrow$ CO$_2$ + H and H + O$_2$ $\rightarrow$ HO$_2$. 
these considerations. Because this uncertainty is difficult to quantify with the simple PAM chamber model and is likely to be significantly overestimated, these uncertainties are not included in the estimated uncertainties of ΔCO/ΔVOC.

SO₂ Analyzer Interference

The accurate measurement of [SO₂] is also integral to the calculation of OH exposure from equation (5) in all OH exposure experiments. Many of the chemical species introduced to the PAM chamber degrade the [SO₂] signal measured by the Thermo Scientific Model 43i-TLE SO₂ Analyzer. This analyzer is supplied with a “hydrocarbon kicker” to scrub VOCs out of the air sample; this preventative measure, however, does not completely mitigate VOC effects on the analyzer measurements. For instance, the SO₂ signal increases by 1.4 to 1.9% for every 100 ppb of m-xylene added to the system. Similarly, the SO₂ signal decreases by 1.6 to 2.3% for every 100 ppb of α-pinene added to the system and 3.5 to 5% for every 100 ppb of isoprene added to the system. Propane, however, had no noticeable effect on the measured [SO₂]. Because the [SO₂] signal is affected by the addition of these VOCs, (SO₂), is measured at the beginning and end of the experiment in the absence of VOCs. This (SO₂), measurement is assumed to remain constant throughout the experiment. It is also assumed that the SO₂ signal measured when the UV lamps are on, (SO₂),, is not affected by this VOC interference because all of the VOC added is assumed to be reacted away when the system reaches equilibrium with the lamps turned on. Therefore, no adjustment is made to the (SO₂), measurements.

The GC-FID and Oxidants

Although the GC-FID has a quantifiable detection limit for the VOCs tested, the method of operation of this instrument is not ideal for the application of the OH counting method. The GC-FID operates by separating H₂, O₂, N₂, CH₄, and CO from the injected sample before measuring remaining carbon compounds, including VOCs. This scrubbed sample is directed to the detector column where the column oven heats the sample at a specified rate. At a particular
time that is unique to each VOC, the compound will elute, creating a peak on a gas chromatogram for analysis. During this measurement process, the VOC to be analyzed can continually react with oxidants and other species not removed from the sample, including OH and O₃. Therefore, the sample from the PAM chamber that is analyzed by the GC-FID has additional time for reactions to occur, creating effects that are not captured in measurements by the other analyzers. Because these results are time-dependent in terms of reactivity, care is taken to ensure that the Teflon analyzer sampling lines are equidistant from the PAM chamber. This effort, however, cannot negate the method of operation of the GC-FID. An O₃ scrubber can be employed to mitigate O₃-initiated reactions in the sample, however, such scrubbers upstream of the GC-FID can cause ghost peaks from the oxidation of the scrubber and other inference with the sample (U.S. EPA, 1998). No scrubbers are used in this experimental setup to remove O₃ or any other species prior to the GC-FID; therefore, all results from the GC-FID used in the determination of ∆VOC underestimate the remaining amount of VOC in the sample once the system has reached equilibrium with the UV lamps turned on.

The GC-FID is used to indicate the presence of all of the VOCs tested in the OH counting method. The GC-FID measurements indicate that no amount of VOC remains in any samples from the PAM chamber down to the detection limit determined for the GC-FID in either the lower or higher light intensity experiments. The simple model of PAM chamber chemistry indicates that no more than 0.1% of any VOC remains for isoprene, m-xylene, and α-pinene for the range of OH exposures obtained for each species through experimentation. This model also indicates, however, that significant amounts or propane remain, up to 24% for the higher light intensity and up to 60% for the lower light intensity. Because of the disagreement between the modeled and experimental OH exposure curves, the GC-FID measurements are assumed to be the most reliable indicator of propane remaining in the PAM chamber; therefore, no adjustment is made to the experimental data or included in the calculation of uncertainties.
Atmospheric Photolysis

The OH counting method is designed to capture the activity of the OH radical through the various reaction paths initiated by VOC oxidation. These atmospheric reaction paths are, however, altered in the PAM chamber by the absence of the full spectrum of atmospheric radiation. In the PAM chamber, the UV lamps supply 254 nm radiation to the chamber specifically for the purpose of producing OH radicals. There are certain products of VOC oxidation, however, that are also lost to atmospheric photodissociation at other wavelengths not present in the chamber. The photolysis of VOC oxidation products, such as acetone (Gierczak et al. 1998), pinonaldehyde (Capouet et al. 2004), formaldehyde (Meller and Moortgat 2000), or glyoxal (Chen and Zhu 2003), can also lead to products that will continue to interact with the OH radical. These processes and reaction paths are not represented in the OH counting method as described here. Therefore, these results are most applicable to the OH radical chemistry in the lower troposphere. Near Earth’s surface, OH radical chemistry will dominate over most photolysis processes because most of the other radiation outside the visible spectrum is absorbed in the upper layers of the atmosphere. Photolysis that does occur, though, is likely to lead to similar reaction products to those produced from OH-initiated oxidation. The photolysis of formaldehyde, for instance, can produce HCO or CO, the same products that are produced by OH-initiated reaction mechanisms. While the yields of the products are likely to vary, the absence of these photolysis processes in the PAM chamber will cause little effect on these results and their applicability to the atmosphere.
4.3 Theoretical Calculations of ΔCO/ΔVOC

Theoretical values for the net number of OH radicals consumed per VOC molecule oxidized are also determined using detailed reaction mechanisms from related literature. The theoretical ΔCO/ΔVOC values are summarized and compared to experimental values in Table 4.2. Theoretical values are determined using gas-phase oxidation mechanisms by counting the number of OH radicals that are consumed and produced down each possible reaction path. The OH count for each reaction path is weighted by the branching ratios associated with that reaction path and summed to obtain an average number of OH radicals consumed by that VOC and its oxidation products per VOC molecule oxidized. All OH interactions with the VOC oxidation

<table>
<thead>
<tr>
<th>VOC</th>
<th>OH-initiated oxidation only</th>
<th>OH and O₃-initiated oxidation</th>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Higher Light Intensity</td>
<td>Lower Light Intensity</td>
<td>Higher Light Intensity</td>
<td>Lower Light Intensity</td>
</tr>
<tr>
<td>propane</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>2.5 – 2.9 (low)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.2 – 2.5 (mid)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.1 – 2.2 (high)</td>
</tr>
<tr>
<td>isoprene</td>
<td>2.3</td>
<td>2.3</td>
<td>2.3</td>
<td>6.3 – 12.5 (low)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.0 – 6.3 (mid)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.4 – 5.0 (high)</td>
</tr>
<tr>
<td>m-xylene</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>7.5 – 20.7 (low)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.1 – 7.5 (mid)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.3 – 6.1 (high)</td>
</tr>
<tr>
<td>α-pinene</td>
<td>1.9</td>
<td>1.9</td>
<td>1.8</td>
<td>4.5 – 6.5 (low)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.8 – 4.5 (mid)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.3 – 3.8 (high)</td>
</tr>
</tbody>
</table>

Table 4.2 Comparison of theoretical and experimental ΔCO/ΔVOC values. Experimental values are estimated from Figures 4.8 and 4.9 and include a range of values for the low (< 200 ppb), mid (200 – 400 ppb), and high (400 – 650 ppb) ranges of VOCs added. These ranges do not include estimates of uncertainty. Theoretical values are calculated using reaction mechanisms from relevant literature.
products are considered until an unexplored pathway or inert product, such as CO$_2$, is encountered. These theoretical estimates do not include OH radical interactions with aerosol.

Based on this theoretical OH counting, propane and its subsequent reaction products are estimated to consume 1.8 OH radicals per propane molecule oxidized using the reaction mechanism proposed by Rosado-Reyes and Francisco (2007) and assuming a dominant RO$_2$ + HO$_2$ → ROOH + O$_2$ pathway and oxidation of ROOH by the OH radical. The additional 0.8 OH radicals consumed are a result of the production of acetone, propanal, and subsequent reaction products. Isoprene and its subsequent reaction products are estimated to consume 2.3 OH radicals using the reaction mechanisms proposed by Archibald et al. (2010), Fan and Zhang (2004), Jenkin et al. (1997), and Spaulding et al. (2003). The additional 1.3 OH radicals consumed by isoprene oxidation products result from the production of methacrolein, methyl vinyl ketone, methylglyoxal, glyoxal, and formaldehyde. m-Xylene and its subsequent reaction products are estimated to consume 3.5 OH radicals using the reaction mechanisms proposed by Bauza-Romero et al. (2007), Gaïl and Dagaut (2006), Hasson et al. (2004), and Zhao et al. (2005). The additional 2.5 OH radicals consumed by m-xylene oxidation products result from the production of glyoxal, methylglyoxal, dimethylphenols, diunsaturated dicarbonyls, and epoxy carbonyls. α-Pinene and its subsequent reaction products are estimated to consume 1.9 OH radicals using the reaction mechanisms proposed by Peeters et al. (2001), Capouet et al. (2004), and Eddingsaas et al. (2012). The additional 0.9 OH radicals consumed by the α-pinene oxidation products result from production of acetone, formaldehyde, pinonaldehyde, and norpinonaldehyde.

Estimates of ΔCO/ΔVOC from these reaction mechanisms are made for NO$_x$-free conditions; therefore, in the proposed schemes, whenever a NO$_x$-only reaction path is encountered, other possible reaction mechanisms are considered. The NO$_x$ reaction paths are most often encountered first in RO$_2$ + NO reactions. In the absence of NO$_x$, RO$_2$ is likely to react with either HO$_2$ or another RO$_2$ as described in Chapter 2. Because of the high level of oxidants in the
PAM chamber, the HO₂ reaction is likely dominant; similarly, the HO₂ reaction is also predicted to be the dominant reaction in the atmosphere in low-NOₓ conditions (Kroll and Seinfeld 2008).

The results in Table 4.1 are used to estimate the number of OH radicals consumed with OH and O₃-initiated oxidation of the tested VOCs. The OH counting for O₃-initiated oxidation is weighted by the percentage of ΔVOC estimated to be consumed by O₃ rather than the OH radical. α-Pinene and its O₃-initiated oxidation products are estimated to consume 0.6 OH radicals per α-pinene molecule oxidized (Capouet et al. 2008), and isoprene and its O₃-initiated oxidation products are estimated to consume 3.4 OH radicals per isoprene molecule oxidized (Fan and Zhang 2004). Because the ozonolysis of α-pinene is known to produce OH radicals at a yield of approximately 0.8 from the direct degradation of the Criegee intermediates, the net consumption of OH radicals is likely to be small even though similar products to OH-initiated oxidation products, such as pinonaldehyde and acetone, are also produced.

Experimental results in Table 4.2 are estimated from the ΔCO/ΔVOC curves for the low (< 200 ppb), mid (200 – 400 ppb), and high (400 – 650 ppb) ranges of VOC mixing ratios added in the PAM chamber. Range cutoffs are arbitrary and do not include uncertainties. Experimental results are presented in ranges rather than in one representative value because the simple model of PAM chamber chemistry indicates that the number of OH radicals is unlikely to stabilize at one value for varying amounts of the VOC added. This OH consumption in the simple model is explored by increasing the residence time in the chamber to the point at which all of the initial VOC added and any subsequent reaction products are consumed. At this limit, the simple model indicates that the number of OH radicals consumed by the VOC and its oxidation products per VOC molecule oxidized decreases as the amount of the VOC added to the system increases. This relationship generally agrees with experimental results. Therefore, it is not reasonable to determine one representative value of ΔCO/ΔVOC for the experimental conditions.

The experimental ΔCO/ΔVOC values in Table 4.2 are determined by estimating the minimum and maximum ΔCO/ΔVOC values over the range of OH exposures associated with the
low, mid, and high ranges of VOC mixing ratios. Values of ΔCO/ΔVOC in the highest OH exposures, or the very low range of VOC mixing ratios, for both light intensities are disregarded because of very large uncertainties as described in Section 4.1.

In general, estimates of the theoretical ΔCO/ΔVOC of propane and m-xylene fall between experimental ΔCO/ΔVOC values for the higher and lower light intensity experiments. Estimates of the theoretical ΔCO/ΔVOC of isoprene and α-pinene, on the other hand, fall in the low range of ΔCO/ΔVOC values for the lower light intensity experiments. The low range of VOC mixing ratios is most applicable to the atmosphere because this range encompasses the typical VOC atmospheric mixing ratios. For the higher light intensity, the low range of experimental ΔCO/ΔVOC values for propane are a factor of 1.4 to 1.6 greater than theoretical ΔCO/ΔVOC estimates, 2.7 to 5.4 for isoprene, 2.1 to 5.9 for m-xylene, and 2.4 to 3.4 for α-pinene. For the lower light intensity, the low range of experimental ΔCO/ΔVOC values for propane is a factor of 0.83 to 0.89 smaller than theoretical ΔCO/ΔVOC estimates and 0.74 to 0.77 smaller for m-xylene. Experimental ΔCO/ΔVOC values in this range for isoprene, however, are a factor of 1.3 to 1.7 greater than theoretical ΔCO/ΔVOC estimates and 1.2 to 1.4 greater for α-pinene.

Sources of Error in Theoretical ΔCO/ΔVOC

The theoretical ΔCO/ΔVOC calculations are likely to overestimate the amount of OH reactions occurring in the PAM chamber because chemical reactions occurring are limited by the residence time of the chamber. The theoretical calculations in Table 4.2, however, assume all possible reactions pathways are exhausted through the production of an inert product or unexplored pathway in the chemical mechanisms from the literature. During an OH exposure experiment, a combination of possible oxidation products is likely to exist at the limit of the residence time in the PAM chamber. This combination of products is determined by reaction rates with the OH radical and competition by other products. On the other hand, theoretical ΔCO/ΔVOC calculations may also be underpredicted because of an incomplete understanding of
each of VOC chemical mechanism that may lead to additional OH radical consumption. Furthermore, the production of HO$_2$ radicals from various reaction mechanisms and the potential for continual OH radical interaction with aerosols is not taken into account in theoretical $\Delta$CO/$\Delta$VOC estimates. These omissions are also likely to lead to an underestimation of the experimental $\Delta$CO/$\Delta$VOC. Which of these effects is likely to dominate, however, is unclear.
Chapter 5

MODELING AND DISCUSSION

Based on the dominant HO\textsubscript{x} chemistry in the PAM chamber, an attempt is made to model this chemistry and the resulting OH exposure for each experiment that is discussed in Chapter 4. This simple PAM chamber chemistry model is described in more detail in this chapter and is used to further explore these reaction mechanisms and as an estimate of uncertainty for several important factors that can affect the OH counting method.

5.1 Description of the Simple PAM Chamber Chemistry Model

This simple model of PAM chamber chemistry is designed primarily for gas-phase chemistry but takes simple aerosol chemical processes into account. This model uses the dominant HO\textsubscript{x} chemistry illustrated in Figure 2.1 to model OH exposure in the PAM chamber. A summary of the significant HO\textsubscript{x} mechanisms and relevant reaction rate coefficients in this simple model is provided in Table 5.1.

The simple PAM chamber model makes several significant assumptions in its treatment of O(\textsuperscript{1}D) and other significant HO\textsubscript{x} components. This model assumes O\textsubscript{3} formation from the reaction O + O\textsubscript{2} (+ M) \rightarrow O\textsubscript{3} (+ M) occurs rapidly, and the destruction of O\textsubscript{3} from photolysis occurs approximately at the rate of O(\textsuperscript{1}D) + H\textsubscript{2}O \rightarrow OH + OH. Furthermore, HO\textsubscript{2} formation from the reactions OH + CO \rightarrow CO\textsubscript{2} + H and H + O\textsubscript{2} \rightarrow HO\textsubscript{2} is assumed instantaneous and thus represented by the rate coefficient for OH + CO. Additionally, the simple model does not initiate photolysis from 185 nm radiation because this radiation is restricted in the PAM chamber.
Table 5.1 Summary of the significant reactions used to model OH exposure in the simple PAM chamber model and reaction rate coefficients. All k-values are calculated for the experimental conditions used, assuming a temperature of 298 K and pressure 2% below atmospheric.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( k_{298K} ) ((\text{cm}^3\text{molecules}^{-1}\text{s}^{-1}))</th>
<th>Note</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O(_3) and HO(_2) Reactions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O + O(_3) (+ M) \rarrow O(_3) (+ M)</td>
<td>1.4 \times 10^{14}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>O(\text{I}) + H(_2)O \rarrow OH + OH</td>
<td>2.0 \times 10^{10}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>O(\text{I}) + N(_2) \rarrow O(\text{I}) + N(_2)</td>
<td>3.1 \times 10^{11}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>O(\text{I}) + O(_2) \rarrow O(\text{I}) + O(_2)</td>
<td>4.0 \times 10^{11}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>OH + OH (+ M) \rarrow H(_2)O(_2) (+ M)</td>
<td>6.1 \times 10^{12}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>OH + O(_3) \rarrow H(_2)O(_2) + O(_2)</td>
<td>7.3 \times 10^{14}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>OH + H(_2)O(_2) \rarrow H(_2)O(_2) + H(_2)O</td>
<td>1.7 \times 10^{12}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>OH + HO(_2) \rarrow H(_2)O + O(_2)</td>
<td>1.1 \times 10^{10}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>HO(_2) + O(_3) \rarrow OH + 2O(_2)</td>
<td>1.9 \times 10^{15}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>HO(_2) + HO(_2) (+ M) \rarrow H(_2)O(_2) + O(_2) (+ M)</td>
<td>3.8 \times 10^{12}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td><strong>VOC and Precursor Reactions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH + CO \rarrow CO(_2) + HO(_2)</td>
<td>2.3 \times 10^{13}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>OH + C(_3)H(_8) \rarrow products</td>
<td>1.1 \times 10^{12}</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>OH + \text{\textalpha\text{-pinene}} \rarrow products</td>
<td>5.3 \times 10^{11}</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>O(_3) + \text{\textalpha\text{-pinene}} \rarrow products</td>
<td>9.0 \times 10^{17}</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>OH + isoprene \rarrow products</td>
<td>1.0 \times 10^{10}</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>O(_3) + isoprene \rarrow products</td>
<td>1.3 \times 10^{17}</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>OH + m-xylene \rarrow products</td>
<td>2.3 \times 10^{11}</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>OH + SO(_2) (+M) \rarrow HOSO(_2) (+M)</td>
<td>9.4 \times 10^{13}</td>
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<tr>
<td><strong>Photolysis</strong></td>
<td></td>
<td></td>
<td>d</td>
</tr>
<tr>
<td>HO(_2) + hv \rarrow OH + O</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>H(_2)O(_2) + hv \rarrow OH + OH</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>O(_3) + hv \rarrow O(_2) + O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ROOR + hv \rarrow products</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>ROOH + hv \rarrow products</td>
<td></td>
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<tr>
<td><strong>RO(_2) and Product Reactions</strong></td>
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</tr>
<tr>
<td>HO(_2) + RO(_2) \rarrow ROOH + O(_2)</td>
<td>2.0 \times 10^{11}</td>
<td>e, f</td>
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<tr>
<td>RO(_2) + RO(_2) \rarrow ROOR + O(_2)</td>
<td>1.0 \times 10^{11}</td>
<td>f</td>
<td></td>
</tr>
<tr>
<td>OH + ROOH \rarrow products</td>
<td>1.7 \times 10^{12}</td>
<td>f</td>
<td></td>
</tr>
<tr>
<td>OH + ROOR \rarrow products</td>
<td>1.7 \times 10^{12}</td>
<td>f</td>
<td></td>
</tr>
<tr>
<td>OH + particle \rarrow products</td>
<td>2.5 \times 10^{11}</td>
<td>f</td>
<td></td>
</tr>
</tbody>
</table>

Note: * NASA JPL, Eval. No. 17, 2011, * Atkinson et al. (2006), ** Atkinson and Arey (2003), * Photolysis frequencies (s\(^{-1}\)) are not recorded in table as these values vary with the light intensity chosen for each experiment, * Boyd et al. (2003), * based on literature including Atkinson (1997), Saunders et al. (2003), Capouet et al. (2004), and others cited here.
An attempt is also made to characterize the general RO₂ chemistry resulting from the oxidation of VOCs. These reactions are simply characterized by the formation and destruction of RO₂, peroxides (ROOH and ROOR), and particles. Possible destruction of the peroxides by photolysis and the OH radical is assumed.

This model is used to construct the OH exposure curves for all of the VOC and CO OH exposure experiments outlined in Table 3.1. During experimentation, the voltage supplied to the lamps is varied to change the light intensity in the chamber; the actual flux of 254 nm radiation, however, is difficult to measure accurately. Therefore, this 254 nm flux is considered an unknown for modeling purposes. To model an OH exposure curve for any precursor gas, the flux first must be determined assuming that all other initial conditions are known. The 254 nm flux is estimated by varying this flux until the initial OH exposure for that light intensity experiment is obtained; this flux is then used to model all OH exposure curves originating from that initial OH exposure. The higher light intensity experiments are modeled with a 254 nm flux of 1.43 x 10¹⁵ photons cm⁻² s⁻¹, and the lower light intensity experiments are modeled with flux of 5.05 x 10¹⁴ photons cm⁻² s⁻¹. In addition to these fluxes, α-pinene experiments are also modeled with 8.93 x 10¹⁴ photons cm⁻² s⁻¹ and 2.30 x 10¹⁴ photons cm⁻² s⁻¹ fluxes for a total of four experimental OH exposure curves. Independent measurements in the PAM chamber estimate this flux to be ~2 x 10¹⁴ photons cm⁻² s⁻¹, which is on the order of estimates obtained using the simple PAM chamber model.

Using the analysis method described in Chapter 2, the number of OH radicals consumed by a VOC and its oxidation products per VOC molecule oxidized is determined by dividing ∆CO by ∆VOC at the same OH exposure. This model is also used to estimate the change in ∆OH at each OH exposure due to differences in reaction rate coefficients between the VOCs and CO. Furthermore, this model is used to investigate the effects of ozonolysis and the production of HO₂ on the OH exposure curves because HO₂ can lead to the regeneration and further consumption of the OH radical via the various HOₓ mechanisms described.
5.2 Modeling OH Exposure, ΔCO/ΔVOC Curves, and Discussion

The simple PAM chamber model is used to simulate the OH exposure experiments for CO, propane, isoprene, m-xylene, and α-pinene. All modeled runs are executed assuming the typical experimental conditions used in the laboratory; therefore, all simulations are run with the following initial conditions: 20% RH, 25°C, 60 ppb SO₂, 12.5 ppm O₃, and 165 s residence time. Furthermore, no wall loss is assumed for any chemical species. The OH exposure for all chemical species is, at a minimum, modeled over the range of experimental OH exposures or over the range of mixing ratios introduced in the PAM chamber. Figure 5.1 displays the modeled and experimental OH exposure curves for CO and the four atmospheric VOCs at each light intensity. A more comprehensible comparison of the modeled and experimental VOC OH exposure curves is found in Appendix A. Figure 5.2 displays the modeled and experimental OH exposure curves for each precursor gas at all light intensities used in experimentation.

At the smallest experimental OH exposure measured with each precursor gas, experimental ΔOH values are greater than modeled ΔOH values by a factor of 1.5 to 10.3 for all experiments with CO and the VOCs. At the higher light intensity, these experimental ΔOH values are greater than modeled ΔOH values by a factor of approximately 2.1 for CO, 8.2 for propane, 3.0 for isoprene, 2.4 for m-xylene, and 4.3 for α-pinene at the lowest OH exposure for each experiment. At the lower light intensity, experimental ΔOH values are greater than modeled ΔOH values by a factor of approximately 1.5 for CO, 5.5 for propane, 2.5 for isoprene, 2.0 for m-xylene, and 3.9 for α-pinene at these OH exposures. For the four α-pinene experiments, experimental ΔOH values are greater than modeled ΔOH values by a factor of approximately 4 for the three highest light intensities and by a factor of 10 for the lowest light intensity experiment. In general, the model best agrees with experimental results for CO and least agrees with experimental results for propane and α-pinene. The model is more successful with modeling CO because the atmospheric oxidation of CO is a simpler and well-understood chemical
Figure 5.1 Modeled and experimental OH exposure curves for CO, propane, isoprene, m-xylene, and α-pinene at the (a) higher light intensity and (b) the lower light intensity. Solid black lines are second-order polynomials fitted to the data with $R^2 > 0.993$ to guide the eye. Dashed lines are modeled OH exposure curves using the simple PAM chamber chemistry model and colored according to the corresponding data.
mechanism. The simplicity of this model, therefore, lends itself to capturing the simpler chemical mechanisms, such as CO, and is not as successful with the general RO₂ and particle chemistry presented to capture the chemical mechanisms for the oxidation products.

The modeled ΔOH for propane is likely to be greatly underestimated because experimental results indicate that the entire amount of propane added is consumed in the PAM chamber to the detection limit of the GC-FID while the model indicates that significant amounts of propane remain. For the smallest experimental OH exposure, the model indicates that 24% of the propane added remains for the higher light intensity and 60% for the lower light intensity. Even in the absence of propane oxidation products that are competition for OH radical consumption, the model indicates that the propane added will not be completely consumed. The model also indicates that no more than 1% of the amount of m-xylene and α-pinene and no more than 0.1% of isoprene added to the PAM chamber remains at either light intensity.

These modeled OH exposure curves are also used to construct ΔCO/ΔVOC curves for the four atmospheric VOCs, and these results are presented in Figures 5.3, 5.4, and 5.5 with the second-order polynomial estimates from the OH exposure data. In general, the model overpredicts the number of OH radicals consumed by an individual VOC and its oxidation products per VOC molecule oxidized (ΔCO/ΔVOC). This follows from the greater underestimation of ΔVOC than ΔCO in the OH exposure curves in Figure 5.1. At the higher light intensity, the model with CO including HO₂ production overpredicts ΔCO/ΔVOC for propane by a factor of approximately 3.9 to 4.3, isoprene by 1.1 to 1.6, and α-pinene by 2.2 to 2.5. Experimental m-xylene ΔCO/ΔVOC is underestimated by the model at the highest OH exposures by a factor of 0.73 but overestimated at the lower OH exposure by a factor of approximately 1.1 to 1.5. At the lower light intensity, the model with CO including HO₂ production overpredicts ΔCO/ΔVOC for propane by a factor of approximately 4.0 to 4.3, isoprene by 1.4 to 2.3, m-xylene by 1.5 to 3.7, and α-pinene by 2.4 to 3.9.
Figure 5.2 Modeled and experimental OH exposure curves for (a) CO, (b) propane, (c) isoprene, and (d) m-xylene at the higher and lower light intensities. The OH exposure curves for (e) α-pinene are displayed for all four experimental light intensities. Solid black lines are second-order polynomials fitted to the data with $R^2 > 0.99$ to guide the eye. Dashed lines are modeled OH exposure curves using the simple PAM chamber chemistry model and colored according to the corresponding data.
Figure 5.3 Modeled and experimental ΔCO/ΔVOC curves for (a) propane, (b) isoprene, (c) m-xylene, and (d) α-pinene at the higher light intensity. Solid lines are ΔCO/ΔVOC curves constructed by OH exposure data that is represented by a second-order polynomial fit (R^2 > 0.995 for all OH exposure curves). Dashed lines are ΔCO/ΔVOC curves constructed by modeled OH exposure data for CO including OH recycling. Dash-dotted lines are ΔCO/ΔVOC curves constructed by modeled OH exposure data for CO assuming no OH recycling.
Figure 5.4 Modeled and experimental ΔCO/ΔVOC curves for (a) propane, (b) isoprene, (c) m-xylene, and (d) α-pinene at the lower light intensity. Solid lines are ΔCO/ΔVOC curves constructed by OH exposure data that is represented by second-order polynomial fit ($R^2 > 0.995$ for all OH exposure curves). Dashed lines are ΔCO/ΔVOC curves constructed by modeled OH exposure data for CO including OH recycling. Dash-dotted lines are ΔCO/ΔVOC curves constructed by modeled OH exposure data for CO assuming no OH recycling.
The experimental $\Delta O_3$ as a function of OH exposure is also modeled using the simple PAM chamber chemistry model. Modeled $\Delta O_3$ for the higher and lower light intensity experiments are displayed in Figure 5.6. Based on the highest OH exposures for each experiment, the experimental $\Delta O_3$ is greater than modeled $\Delta O_3$ by a factor of 1.3 to 1.6 for both the higher and lower light intensity experiments. The model also predicts a significant difference in the slopes of the $\Delta O_3$ as a function of OH exposure between the calibration gas and the hydrocarbons. The $\Delta O_3$ for CO exhibits a significantly different slope than that of the VOCs because of the modeled HO$_2$ production from the CO + OH mechanism. The slope of $\Delta O_3$ for each hydrocarbon, however, varies little over the range of applicable OH exposures. The model does reasonably predict the slope of $\Delta O_3$ data for CO and propane, though not the magnitude of O$_3$ consumed.

In general, this PAM chamber chemistry model estimates significantly more OH radical consumption in both the OH exposure and $\Delta CO/\Delta VOC$ curves than what is observed in experimental results. This disagreement is observed even in the OH exposure curves for the calibration gas, CO, that has a well-understood atmospheric degradation mechanism. The failure of the model in even simple reaction mechanisms is explored by an attempt to use optimization techniques to indicate which variables already existing in the model have an impact on the failure of the model. Optimized parameters include residence time, 254 nm flux, all reaction rate coefficients, and an OH radical wall loss. These efforts, however, do not lead to an explicit explanation for the failure of the model. The optimization of the model parameters is not able to reconcile modeled results to experimental results for both $\Delta OH$ and $\Delta O_3$ as a function of OH exposure, although optimization for $\Delta OH$ alone is possible.

Although the simple PAM chamber chemistry model does not reasonably predict the OH exposure for any precursor gas used to test the OH counting method, this model may be useful in a relative sense. Therefore, the simple PAM chamber model is used to estimate the relative uncertainty due to differences in reaction rate coefficients, in the exploration of HO$_x$ chemical
Figure 5.5 Modeled and experimental $\Delta CO/\Delta VOC$ curves for the (a) higher light intensity and (b) lower light intensity. Solid lines are $\Delta CO/\Delta VOC$ curves constructed by OH exposure data that is represented by a second-order polynomial fit ($R^2 > 0.993$ for all OH exposure curves). Dashed lines are $\Delta CO/\Delta VOC$ curves constructed by modeled OH exposure data for CO including OH recycling.
Figure 5.6 Modeled and experimental ΔO₃ curves plotted as a function of OH exposure for the (a) higher light intensity and (b) lower light intensity. Experimental data are indicated with uncertainties by the colors and shapes in the legend. Modeled ΔO₃ are indicated by the dashed lines in associated colors to experimental data.
mechanisms and their effect on $\Delta OH$ and $\Delta O_3$ as a function of OH exposure, and in the analysis of $\Delta CO/\Delta VOC$ curves, all discussed in Chapter 4.

More sophisticated modeling efforts have been employed to simulate OH exposure curves by a postdoctoral scientist, Dr. Shuang Chen, at the Pennsylvania State University (manuscript in preparation). Detailed VOC chemical mechanisms are used to better estimate the interactions of VOC oxidation products in the PAM chamber. While certain representations of OH exposure for CO and other VOCs show promise in simulating experimental data using these detailed mechanisms, some also demonstrate significant disagreement. Therefore, it is unclear if the simple PAM chamber model needs further refinement to adequately simulate these OH counting PAM chamber experiments.
Chapter 6

CONCLUSIONS

Based on atmospheric HO₃ chemistry, a laboratory-based OH radical counting method is developed to measure the number of OH radicals consumed by an atmospheric VOC and subsequent oxidation products per VOC molecule oxidized in the highly oxidizing environment of the PAM chamber. Experimental, modeling, and theoretical efforts are used to determine and characterize OH radical consumption for propane, isoprene, m-xylene, and α-pinene by using the simple oxidation chemistry of CO as a calibration gas for comparison. Significant results and conclusions obtained from these experiments are summarized and expanded upon in this chapter to conjecture on the future research arising from this work.

6.1 Concluding Thoughts

The OH exposure experiments are conducted first to obtain relationships between the number of OH radicals consumed and OH exposure for different precursor gases, including four VOCs and a calibration gas. The OH exposure experiments conducted for α-pinene demonstrate the construction of these OH exposure curves and dependence of OH exposure on the light intensity in the PAM chamber. As the light intensity increases, more OH radicals are created in the PAM chamber, leading to higher OH exposures. The OH exposure experiments conducted for the five atmospheric precursor gases indicate that m-xylene and its oxidation products consume the greatest number of OH radicals, followed by isoprene, α-pinene, propane, and finally CO for the higher light intensity. The same general result is found for the lower light intensity, though whether isoprene or m-xylene consume more OH radicals is less clear.
Applying the OH counting method to these OH exposure curves, the same result can be obtained and quantified by calculating $\Delta CO/\Delta VOC$, or the number of OH radicals consumed by a VOC and subsequent oxidation products per VOC molecule oxidized. Theoretical, experimental, and modeled $\Delta CO/\Delta VOC$ values are summarized in Table 6.1. Modeling efforts demonstrate that $\Delta CO/\Delta VOC$ cannot be represented by one value; therefore, ranges of the experimental and modeled $\Delta CO/\Delta VOC$ are presented for low, mid, and high range levels of the VOC added. Theoretical estimates include OH-initiated oxidation only because the impact of ozonolysis on OH counting is small, at worst less than 10% for $\alpha$-pinene at the lower light intensity.

Experimental and modeled results agree that there is a maximum in $\Delta CO/\Delta VOC$ at

<table>
<thead>
<tr>
<th>VOC</th>
<th>Theoretical OH-initiated oxidation only</th>
<th>Experimental Higher Light Intensity</th>
<th>Experimental Lower Light Intensity</th>
<th>Modeled Higher Light Intensity</th>
<th>Modeled Lower Light Intensity</th>
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</thead>
<tbody>
<tr>
<td>propane</td>
<td>1.8</td>
<td>2.5 – 2.9 (low)</td>
<td>1.5 – 1.6 (low)</td>
<td>6.5 – 11.4 (low)</td>
<td>3.8 – 7.0 (low)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.2 – 2.5 (mid)</td>
<td>1.3 – 1.5 (mid)</td>
<td>4.5 – 6.5 (mid)</td>
<td>2.5 – 3.8 (mid)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.1 – 2.2 (high)</td>
<td>1.2 – 1.3 (high)</td>
<td>3.3 – 4.5 (high)</td>
<td>1.9 – 2.5 (high)</td>
</tr>
<tr>
<td>isoprene</td>
<td>2.3</td>
<td>6.3 – 12.5 (low)</td>
<td>3.0 – 4.0 (low)</td>
<td>6.6 – 13.9 (low)</td>
<td>4.0 – 9.3 (low)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.0 – 6.3 (mid)</td>
<td>2.4 – 3.0 (mid)</td>
<td>4.7 – 6.6 (mid)</td>
<td>2.7 – 4.0 (mid)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.4 – 5.0 (high)</td>
<td>2.1 – 2.4 (high)</td>
<td>3.5 – 4.7 (high)</td>
<td>1.9 – 2.7 (high)</td>
</tr>
<tr>
<td>m-xylene</td>
<td>3.5</td>
<td>7.5 – 20.7 (low)</td>
<td>2.6 – 2.7 (low)</td>
<td>7.1 – 15.2 (low)</td>
<td>4.1 – 10.3 (low)</td>
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<td></td>
<td></td>
<td>6.1 – 7.5 (mid)</td>
<td>2.4 – 2.6 (mid)</td>
<td>4.9 – 7.1 (mid)</td>
<td>2.7 – 4.1 (mid)</td>
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<tr>
<td></td>
<td></td>
<td>5.3 – 6.1 (high)</td>
<td>2.3 – 2.4 (high)</td>
<td>3.6 – 4.9 (high)</td>
<td>2.1 – 2.7 (high)</td>
</tr>
<tr>
<td>$\alpha$-pinene</td>
<td>1.9</td>
<td>4.5 – 6.5 (low)</td>
<td>2.2 – 2.5 (low)</td>
<td>6.7 – 14.2 (low)</td>
<td>3.8 – 9.4 (low)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.8 – 4.5 (mid)</td>
<td>1.8 – 2.2 (mid)</td>
<td>4.7 – 6.7 (mid)</td>
<td>2.5 – 3.8 (mid)</td>
</tr>
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<td></td>
<td></td>
<td>3.3 – 3.8 (high)</td>
<td>1.6 – 1.8 (high)</td>
<td>3.5 – 4.7 (high)</td>
<td>1.7 – 2.5 (high)</td>
</tr>
</tbody>
</table>
higher OH exposures, followed by a general decrease in $\Delta CO/\Delta VOC$ as OH exposure decreases and the VOC mixing ratio increases in the chamber. This trend may be caused by a change in the OH interactions as OH exposure decreases. Under conditions when only small amounts of VOCs are present in the chamber, a relatively smaller fraction of OH radicals are consumed by the initial VOC. Thus, with relatively more OH radicals and high OH exposures, the frequency of OH radical interactions with VOC oxidation products increases. This may also explain why $\Delta CO/\Delta VOC$ values are approximately a factor of two greater in the higher light intensity experiments than in lower light intensity experiments. Furthermore, OH radicals may be depleted by the continual process of aerosol aging. It is likely that when high levels of VOCs are added to the chamber, more aerosols are produced, making less mass accessible to OH oxidation. Therefore, these processes make it probable that more OH radicals are consumed per VOC molecule oxidized at higher OH exposures and that this OH consumption decreases as the amount of VOC added increases and OH exposure decreases.

Modeled $\Delta CO/\Delta VOC$ significantly overestimates experimental $\Delta CO/\Delta VOC$ by a factor of approximately 1.1 to 4.3 for the higher light intensity, though $m$-xylene is actually underestimated at some OH exposures, and 1.4 to 4.3 for the lower light intensity for the four VOCs tested when comparing values at each OH exposure. When comparing the ranges of $\Delta CO/\Delta VOC$ for each range of VOC addition in Table 6.1, however, the model agrees reasonably well with some experimental results. For the higher light intensity, the model estimates similar OH consumption ranges for the low and mid range estimates for isoprene and $m$-xylene. For the lower light intensity, the model estimates similar OH consumption ranges for the high range estimates of isoprene and $m$-xylene. The large uncertainties and generally strong disagreement between the model and experimental $\Delta CO/\Delta VOC$ in the low range VOC estimates may limit the usefulness of this technique for typical atmospheric mixing ratios of these VOCs.

In conclusion, modeling efforts are unsuccessful at reproducing the magnitude of $\Delta OH$, $\Delta O_3$, and $\Delta CO/\Delta VOC$ as a function of OH exposure but are more successful at simulating the
impacts of certain effects on OH exposure curves. For instance, the model captures the approximate slopes of the experimental $\Delta O_3$ curves for both CO and propane and simulates an impact of ozonolysis on OH exposure similar to what is observed in experimentation. Further modification and enhancement of the simple PAM chamber chemistry model, however, is necessary to resolve the significant disagreements between experimental and modeled data, particularly in the simulations with the calibration gas and treatment of the modeled products.

6.2 Future Work

The results of these OH exposure experiments and the conclusions from testing the OH counting method introduce many new avenues of research. The sensitivity of the experimental setup and uncertainties in OH exposures should be improved to better quantify OH radical consumption for atmospherically relevant mixing ratios. Then, assuming its usefulness, the OH counting method can be applied to a larger profile of atmospheric VOCs to determine the impact of these VOCs on OH radical consumption in the atmosphere. Potential VOCs might include mesitylene (1,3,5-trimethylbenzene), toluene, cyclohexane, limonene, $\beta$-pinene, $p$-xylene, $o$-xylene, or $n$-decane. Based on laboratory work concurrent to the OH exposure experiments, discretion is necessary when applying the OH counting method to certain atmospheric VOCs. The VOCs that react slowly with the OH radical are not practical for these experiments because the amount of the VOC consumed may be difficult to detect. Therefore, VOCs such as CH$_4$, that have a rate coefficient of $6.3 \times 10^{-15}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at 298 K (NASA JPL Eval. No. 17, 2011), would not be ideal candidates for the OH counting method as described here. Furthermore, such VOC experiments are highly dependent on GC-FID measurements for the construction of the OH exposure curves. Certain VOCs with low vapor pressures, such as $n$-decane, also may not be ideal for use in the OH counting method. Low vapor pressures can lead to condensation on the walls of the PAM chamber and this type of wall loss will significantly impact the atmospheric chemistry simulated in the PAM chamber.
Further experimentation is also necessary to characterize the impact of the chosen initial conditions on the OH counting method. Altering the RH, residence time, 254 nm flux, and O$_3$ concentration can significantly change the measured OH exposure in many ways. While the results of OH exposure experiments indicate that the number of OH radicals consumed increases with the 254 nm flux, no experiments are carried out to explore the impact of varying these other conditions on ΔCO/ΔVOC. Theoretically, varying these conditions should have little impact on ΔCO/ΔVOC because these conditions should alter each OH exposure curve proportionally. Effects that are not well quantified in the PAM chamber, however, such as the impact of light intensity and wall interactions on the VOC and product chemistry, may impact OH exposure curves differently. Furthermore, increasing the average residence time in the PAM chamber will allow for additional product chemistry to occur, effectively altering the ΔOH and OH exposure relationship as well. By changing the ambient O$_3$ concentration in the PAM chamber, the impact of ozonolysis on the OH exposure curves for VOCs, such as isoprene and α-pinene, will also change.

These OH exposure experiments are conducted for applicability in a NO$_x$-free environment. These experiments, however, could be extended to encompass high-NO$_x$ and low-NO$_x$ conditions as well to quantify OH radical consumption for NO$_x$-dependent environments. Consequent modeling efforts are also possible as general and specific OH-initiated NO$_x$ oxidation schemes are available for all of the VOCs tested in this work as well as many other significant atmospheric VOCs. Moreover, other calibration gases can also be explored for these or HO$_x$-only conditions.

Further research is also required to reconcile experimental and modeled results for ΔOH, ΔO$_3$, and ΔCO/ΔVOC as a function of OH exposure. Significant progress can be made by first resolving the failure of the model in constructing OH exposure curves for CO. Because CO has a well-understood atmospheric oxidation mechanism but cannot be reasonably modeled, ensuring that the fundamental HO$_x$ and PAM chamber chemistry can construct the experimental OH
exposure curves may improve the modeling of OH exposure curves for all precursor gases and estimates of ΔCO/ΔVOC. Modeling of the VOC OH exposure curves can also be enhanced by using chemical mechanisms specific to each VOC such as those used in the theoretical ΔCO/ΔVOC calculations in this work and by postdoctoral scientist, Shuang Chen. Experimental results may also prove to be useful in improving such chemical mechanisms from the literature.
APPENDIX A

VOC OH Exposure Curves
Figure A.1 OH exposure curves for propane, isoprene, m-xylene, and α-pinene at the (a) higher light intensity and (b) lower light intensity. Solid black lines are second-order polynomials fitted to the data with $R^2 > 0.993$ to guide the eye. Dashed lines are modeled OH exposure curves using the simple PAM chamber chemistry model and colored according to the corresponding data.
REFERENCES


