Chapter 1

INTRODUCTION

1.1 Background and Motivation

Earth's atmosphere can be roughly imagined as a slow-burning flame, gradually oxidizing its chemical constituents in a series of reactions driven largely by ozone (O_3) and families of oxide radicals. In the troposphere, two such families drive the ambient oxidative chemistry: HO_x (= OH + HO_2) and NO_x (= NO + NO_2). These radical pairs are described as families because of their rapid cycling; species within chemical families interconvert much more rapidly than they are produced or destroyed. The HO_x family typically initiates oxidation by the reaction of reduced compounds with OH, a highly reactive radical formed following the photolysis of ozone, while the NO_x family efficiently propagates radical chain reactions and leads to ozone formation. The abundance and cycling of these radical families together set the timescale of oxidation and determine the reactive fate of other chemicals in the troposphere (Seinfeld and Pandis, 2006).

Among the most abundant of the other chemicals with which radical families may react are volatile organic compounds (VOCs), which act as fuel for the atmosphere's slow-burning flame. VOCs are emitted from a variety of sources, both biogenic and anthropogenic, and their oxidation in the atmosphere can be initiated *via* two main pathways: the abstraction of a hydrogen atom by OH, or the addition of OH, O_3, NO_3, or Cl to a double bond. In each case, an alkyl radical species in formed, which then undergoes a series of radical-propagating reactions, illustrated for methane in Figure 1.1, ultimately resulting in the formation of stable oxidized species such as CO_2.

Alkyl radicals formed in the oxidation of VOCs typically add O_2 to form peroxy radicals, denoted RO_2 (*e.g.* $CH_3OO^{\cdot}$ in Figure 1.1). These peroxy radicals represent a branching point in the oxidative mechanism: depending on the ambient conditions, they may react with other peroxy radicals, NO, or HO_2, or isomerize before reacting. The relative prominence of these pathways frequently determines the chemical products of the overall VOC oxidation mechanism. For example, reaction with NO may lead to greater ozone production through the formation and photolysis of NO_2, while reaction with HO_2 may lead to the formation of hydroperoxides and

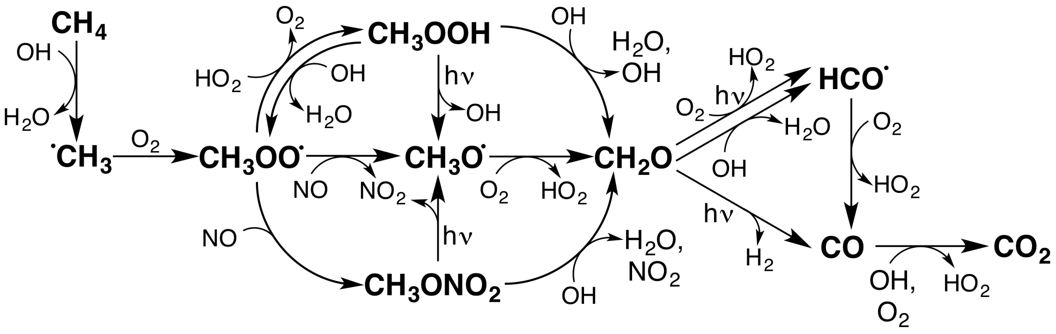

Figure 1.1: Steps in the atmospheric oxidation of methane. The relative abundance of NO_x and HO_x controls not just the fate of the $CH_3OO^{\cdot}$ radical, but also the total radical cycling and ozone formation from VOC oxidation. Thus, the overall net reaction under NO-dominant conditions, and including subsequent photolysis of NO_2 and other reactions, is $CH_4 + 10O_2 \rightarrow CO_2 + H_2O + 5O_3 + 2OH$, while the net reaction under HO_2-dominant conditions is $CH_4 + 2OH + 2O_2 \rightarrow CO_2 + 2H_2O + 2HO_2$, assuming CH_2O photolyzes to form HCO in either case (Jacob, 1999).

other less-volatile species. Under conditions of low anthropogenic influence (*i.e.* low NO_x), the reactive fate of peroxy radicals is dominated by HO_2, which is the primary focus of the work included in this thesis.

Whatever the fate of the peroxy radicals, the chemical products resulting from VOC oxidation include many species commonly referred to collectively as “smog,” which can have a wide range of adverse effects when present even in trace quantities. Ozone, for example, is a commonly regulated pollutant around the world (EPA, 2015), known to cause premature mortality and a variety of disease responses in humans (Bell *et al.*, 2006; Jerrett *et al.*, 2009; Li *et al.*, 2016), negatively impact plant health (Chameides *et al.*, 1994; Fuhrer, 2002; Zinser *et al.*, 2000), and contribute to radiative climate forcing in the troposphere (Pachauri *et al.*, 2014; Worden *et al.*, 2008). VOC oxidation typically constitutes the dominant source of local ozone pollution (Jacob, 1999); a detailed understanding of VOC oxidation mechanisms is therefore imperative to accurately assess and forecast ozone formation.

When VOC oxidation produces compounds with sufficiently low volatility, such species can then condense onto suspended ambient particles (or nucleate new particles) to form secondary organic aerosol (SOA), another component of smog. Like ozone, tropospheric particulate matter is harmful to human health; epidemiological studies suggest that particulate pollution contributes annually to over 4.2 million premature deaths worldwide (Cohen *et al.*, 2017; Lelieveld *et al.*, 2015; Nel, 2005; Pope *et al.*, 2002; Pope *et al.*, 2009; Pope and Dockery, 2006), and targeted studies have shown specific adverse effects of particles within the respiratory and circulatory systems (Gaschen *et al.*, 2010; Künzi *et al.*, 2015; Nelin *et al.*, 2012). Aerosols also affect visibility (Watson, 2002) and play a prominent but uncertain role in climate forcing through their direct radiative properties as well as their indirect impacts *via* cloud formation (Myhre *et al.*, 2013; Raes *et al.*, 2010). Globally, a large and highly variable portion (20-90%) of particulate mass below 2.5 μm in diameter consists of organic material (Murphy *et al.*, 2006; Zhang *et al.*, 2007), and a significant fraction (30-95%) of that organic aerosol is SOA (Jimenez *et al.*, 2009; Zhang *et al.*, 2007), implying that the oxidation of VOCs can exert a strong influence on particulate mass budgets.

Although over 10,000 unique organic compounds may exist in the atmosphere (Goldstein and Galbally, 2007), each with its own oxidation mechanism and smog formation potential, one particular VOC holds outsized significance for its sheer abundance: 2-methyl-1,3-butadiene, or isoprene. Isoprene is emitted primarily by deciduous plants in quantities exceeding 500 Tg y^{-1}, comprising approximately a third of the total VOC emissions to the atmosphere (Guenther *et al.*, 2012), and is oxidized rapidly in the troposphere ($\tau \sim 1$ h), primarily by the addition of OH to one of its double bonds (Atkinson and Arey, 2003b). The subsequent chemistry by which isoprene-derived radicals and VOCs react in the atmosphere forms a highly complex mechanism, with numerous distinct branching pathways and hundreds of stable products (Jenkin *et al.*, 2015). In recent years, a combination of field observations, chamber experiments, quantum calculations, and modeling – including some of studies contained in this thesis – has substantially improved our knowledge of these complex oxidation mechanisms, providing valuable insight into the effects of isoprene on HO_x and NO_x cycling, ozone production, SOA formation, and other important aspects of air quality and atmospheric chemistry.

In regions with abundant isoprene emissions, including the the Amazon, the southeast United States, and other highly productive tropical and temperate forests, the chemistry of isoprene oxidation alone can effectively determine the oxidative capacity of the atmosphere and contribute the majority of local O_3 and SOA production. Such areas are typically located away from major anthropogenic pollution sources, leading to relatively low levels of NO; as such, reaction with HO_2 represents the predominant fate of most peroxy radicals formed in the oxidation mechanism (although rapid isomerization has recently been shown to compete in some cases, *e.g.* Crounse *et al.*, 2011, Peeters *et al.*, 2014, and Teng *et al.*, 2017). In the

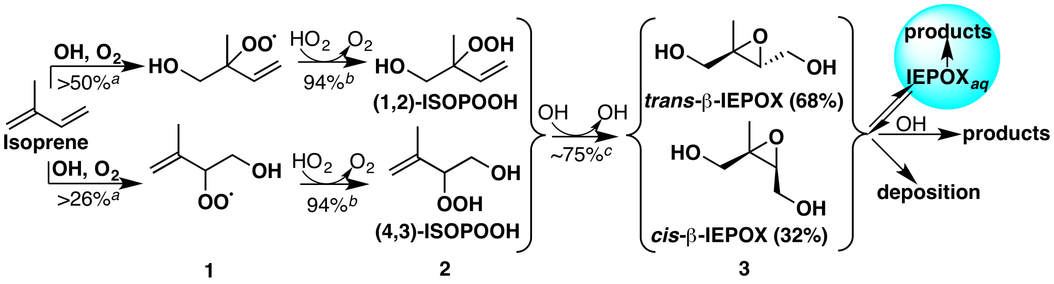

Figure 1.2: Dominant reaction channels in the oxidation of isoprene under HO_2-dominated conditions. Reported yields are from [a]Teng *et al.* (2017), [b]Liu *et al.* (2013), and [c]Appendix D. The reported isoprene peroxy radical yields are given at the kinetic limit of short RO_2 lifetimes, but under most ambient conditions, the dynamic equilibration between peroxy radicals will produce much higher yields of the β isomers shown. The isomers shown are therefore estimated to comprise >95% of the total ISOPOOH and IEPOX formed in the atmosphere (see Chapters 2 and 4).

HO_2-dominated isoprene oxidation mechanism (the major steps of which are shown in Figure 1.2), the initial isoprene hydroxy peroxy radicals (**1**) react with HO_2 to produce isoprene hydroxy hydroperoxides (ISOPOOH, **2**) in high yields (Liu *et al.*, 2013; Paulot *et al.*, 2009a). The predominant ISOPOOH isomers can then add another OH and rapidly react to form a dihydroxy epoxide (IEPOX, **3**), recycling one equivalent of OH in the process. This unique rearrangement was only recently discovered (Paulot *et al.*, 2009b) thanks to instrumental advances enabling the differentiation of isobaric ISOPOOH and IEPOX.

The subsequent fate of IEPOX in the atmosphere has been the subject of intense scrutiny, and is addressed in multiple chapters in this thesis. It is known to react with OH, deposit onto surfaces, or undergo reactive uptake onto particles, but the relative contributions of these pathways and their eventual consequences were, until recently, largely unknown. Because IEPOX is produced in ~70% overall yield (Liu *et al.* (2013) and Appendix D) from isoprene under HO_2-dominated conditions, and ~30% yield globally when non-HO_2 pathways are included (4, characterizing the fate of IEPOX is of vital importance for determining how the HO_2-dominated pathway affects oxidant cycling and contributes to the production of ozone and SOA. A better understanding of IEPOX will be an integral piece of the broader question: how does isoprene influence air quality and the oxidative chemistry of the troposphere, and what role does the HO_2-dominated pathway play in this effect?

1.2 Content

The work included in the chapters and appendices of this thesis represents my efforts to answer this question through a variety of research projects and methods. In the course of my work, I have employed three key tools of atmospheric chemical research: laboratory studies, generally in the form of environmental chamber experiments; fieldwork, or the measurement of ambient atmospheric chemical conditions; and modeling, using either idealized box models or global chemical transport models to simulate the chemistry in question. The interaction of these three methods in the field of atmospheric chemistry has enabled remarkable success in the identification, understanding, and mitigation of such important issues as urban air pollution and stratospheric ozone depletion (Abbatt *et al.*, 2014; Burkholder *et al.*, 2017; Melamed *et al.*, 2015). As each tool relies on the insights ascertained from the others to inform their own analysis and direction, it is through their application in tandem that meaningful conclusions are reached and the field advances. Some of the projects included in each chapter here focus on just one of these three pillars; most employ some elements of each. Detailed descriptions of experimental techniques can be found in each chapter, but a brief overview of the three key methods is presented here, followed by an outline of the rest of the thesis.

1.2.1 Laboratory Studies

Laboratory studies represent our primary means of characterizing the fundamental processes underlying the chemistry of the atmosphere. The most widely used laboratory method is the environmental chamber experiment, or the isolation of a volume of air inside a reaction vessel (*e.g.* a large Teflon bag); Chapters 2, 3, and 5 in this thesis all employ chamber studies, as do Appendices A-F. Chamber experiments are designed to pinpoint a specific chemical process in a regulated environment, without interference from the confounding factors present in ambient air. By controlling as many variables as possible, chamber studies allow researchers to identify and measure the process in question more accurately and precisely than they could in the field, and to systematically vary chamber conditions to the factors influencing that process.

In a typical experiment, reactants of interest are first introduced to the chamber and, following a brief stabilization and mixing period, exposed to the desired reactive chemical environment. These reactive conditions may include ultraviolet light for the study of photolysis; chemical oxidants, such as ozone or OH; or seed particles onto which a compound may condense. Air from the chamber is then drawn into various instruments to measure relevant properties of the gas and particle phases. Specific instruments are described in greater detail in each chapter, but among the most commonly used instrumental methods in this thesis are gas chromatography (GC), chemical ionization mass spectrometry (CIMS), aerosol mass spectrometry (AMS), and scanning mobility particle sizing (SMPS). The GC and CIMS measure concentrations of gaseous species; our GC is primarily sensitive to hydrocarbons, while the CF_3O^- reagent ion in our time-of-flight and triple-quadrupole CIMS most efficiently ionizes compounds with strong dipoles or high polarizability (Crounse *et al.*, 2006; St. Clair *et al.*, 2010), making them complementary measurement techniques. The AMS (Jayne *et al.*, 2000) and SMPS (Wang and Flagan, 1990) detect the chemical composition and size distribution, respectively, of sub-micron particles suspended in the chamber.

Although chamber experiments have been a mainstay of atmospheric laboratory studies for many decades, recent advances have opened new avenues of study for this dependable method. Among those employed in this thesis are novel pathways for the synthesis of reactants previously unavailable for chamber experimentation, including IEPOX (Chapters 2 and 5) and other late-generation isoprene oxidation products (Chapter 3), and new instrumentation, including a coupled GC-CIMS capable of separating isobaric compounds that were previously indistinguishable (Chapters 2 and 3, and Appendices A, B, and D).

The ubiquity of chambers in atmospheric laboratories has spurred extensive characterization of their properties and the techniques employed in such experiments (see, *e.g.*, Schwantes, 2017 for the Caltech environmental chambers, and Cocker *et al.*, 2001, Carter *et al.*, 2005, and Wang *et al.*, 2011 for others). Still, chamber experiments have important limitations that can confound the interpretation of their data. Some such limitations, including the losses of particles to chamber walls (Crump and Seinfeld, 1981; McMurry and Rader, 1985), have been carefully parameterized (Hildebrandt *et al.*, 2009; Hildebrandt *et al.*, 2011; Loza *et al.*, 2014; Loza *et al.*, 2012; Weitkamp *et al.*, 2007), while others remain poorly understood, including the losses of gaseous species to surfaces in chambers and instruments (Bernhammer *et al.*, 2017; Matsunaga and Ziemann, 2010a; Rivera-Rios *et al.*, 2014; Zhang *et al.*, 2015). While chamber experiments remain our primary method for understanding the fundamental chemistry of the atmosphere, field measurements and modeling are necessary to ensure that the processes studied in the laboratory are well understood and atmospherically relevant.

1.2.2 Field Studies

Another longstanding cornerstone of atmospheric research is the *in situ* measurement of ambient gases, particles, and meteorological conditions. Fieldwork is vital for determining the relevance and significance of known chemical processes in the atmosphere, and for identifying new avenues of research. It is only by observing the actual atmosphere, and comparing those measurements to laboratory data and simulations, that we can establish how well we understand the chemistry that occurs in ambient conditions and what previously unexplored processes may be important. As an example relevant to the contents of this thesis, it was, in large part, observations of oxidant recycling and unexplained particulate organic matter (such as C_5 tetrols) in the Amazon and other isoprene-rich areas that spurred further research into the oxidative chemistry and potential SOA production of isoprene under low-NO conditions (Claeys *et al.*, 2004; Karl *et al.*, 2007; Kleindienst *et al.*, 2009; Kleindienst *et al.*, 2007; Kuhn *et al.*, 2007; Lelieveld *et al.*, 2008; Tan *et al.*, 2001).

Data from two primary types of field study – stationary and airborne measurements – are used in this thesis. Both employ a wide variety of instruments, including those described above in Section 1.2.1, assembled on some form of research platform. In stationary field campaigns, the research platform is usually a tower, on which instruments can sample air at one or more vertical levels of interest. This enables measurements of the variability at a single site caused by changing conditions through time – *e.g.* temperature, insolation, wind direction, humidity, etc. – but limits the breadth of the campaign to conditions experienced exclusively at that site. The stationary campaigns that feature in this thesis include Green Ocean Amazon (GOAmazon, Appendix G), which studied the interaction of remote Amazonian airmasses with the urban plume from the Brazilian city of Manaus between January 2014 and December 2015, and the Southern Oxidant and Aerosol Study (SOAS, Chapter 3 and Appendices A and E), which investigated similar biogenic-anthropogenic interactions from a smaller tower in Centreville, Alabama between June and July of 2013.

Airborne field campaigns, in which instruments are loaded into the body of an airplane and sample air through external ports in flight, enable the sampling of a wider variety of altitudes and conditions that can be accessed by plane, but at the expense of observing the temporal evolution of those conditions. This thesis uses data from airborne measurements collected as part of GOAmazon (Appendix G) and from a series of small campaigns investigating oceanic aerosol and cloud composition in coastal California (Appendix H) during the summers of 2011 (Eastern Pacific Emitted Aerosol Cloud Experiment, E-PEACE; Russell *et al.*, 2013), 2013 (Nucleation in California Experiment, NiCE; Coggon *et al.*, 2014) and 2015 (Biological and Oceanic Atmospheric Study, BOAS).

1.2.3 Modeling

Finally, the advent of improved computing power has enabled researchers to carry out simulations that can quickly and effectively model the chemistry that occurs in laboratory studies and in the field. These modeling capabilities are a powerful tool for determining whether known chemical processes can accurately describe the results of chamber experiments or the observations of field campaigns, and if not, for potentially diagnosing the sources of those inaccuracies. The ease with which such complex simulations can be performed makes them attractive for a wide range of applications, but models have their own limitations; chiefly, they are only as good as the chemistry that goes into the them, and when they do not align with observations, it can be difficult (if not impossible) do determine what aspects of that chemistry are wrong. Additionally, when models encompass wider parameter spaces (*e.g.* increasing to a global scale, including meteorology and emissions, etc.), and when they employ simplified chemical mechanisms, their potential for error widens substantially (Knote *et al.*, 2015).

Two major varieties of simulations are employed in the work included in this thesis: box models and chemical transport models (CTMs), each with their own applications and limitations. Box modeling refers to the zero- or one-dimensional (time-dependent) simulation of chemical reactions of well-mixed constituents, and is particularly useful for comparison with chamber experiments to determine whether the measured or estimated rates and products of a given process align with observations. The complexity and scope of box models spans a wide range, from simple custom-made simulations for individual experiments to more sophisticated and widely available models, such as the Master Chemical Mechanism (MCM; Jenkin *et al.*, 2015), the Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A; Aumont *et al.*, 2005), the Framework for 0-D Atmospheric Modeling (F0AM; Wolfe *et al.*, 2016), and the Gas-Aerosol Model for Mechanism Analysis (GAMMA; McNeill *et al.*, 2012 and Woo and McNeill, 2015), some of which contain thousands of chemical reactions. In this thesis, Chapter 4 discusses the compilation of an explicit isoprene oxidation box model, while Appendices D, E, and G make extensive use of subsets of the isoprene model to compare against observations.

Chemical transport modeling takes a usually simplified version of the same chemical mechanism and expands the domain to four dimensions, taking into account the spatial distribution of the relevant chemicals by integrating meteorology and simulating their evolution through time and space, frequently on a regional or global scale. In so doing, CTMs give insight into how the chemistry measured in chambers and in field studies plays out in the broader context of the atmosphere at large, thus providing some idea of the overall importance of that chemistry. In this thesis, Chapter 3 and Appendices B, D, and G make use of this capacity with GEOS-Chem (Bey *et al.*, 2001; Mao *et al.*, 2013), a widely used CTM, while Chapter 4 discusses the development of a new isoprene mechanism for GEOS-Chem.

1.2.4 Outline

The following chapters and appendices of this thesis describe the individual research projects to which I have contributed toward the goal of identifying the chemical mechanisms by which isoprene can influence ambient oxidant cycling, particle formation, and the concentrations of various VOCs, especially *via* the IEPOX formation pathway that occurs under HO_2-dominated conditions. While the chapters relate in this overarching goal, they are written to stand alone as published manuscripts (or, in the case of Chapter 4, a manuscript in preparation). The projects most directly related to the HO_2-dominated oxidation of isoprene, and to which I most substantially contributed, are included as chapters, while the appendices, arranged chronologically, represent more tangentially related projects on which I served as a coauthor.

Chapters 2 and 3 describe experiments designed to investigate the fate of IEPOX in the gas phase. As described above, IEPOX is produced in high yields from the reaction of OH with ISOPOOH (described in Appendix D), which is itself a first-generation oxidation product of isoprene under HO_2-dominated conditions. IEPOX can either be oxidized (primarily by OH) in the gas phase, deposit onto surfaces, or undergo reactive uptake onto particles and contribute to SOA mass. Because of the ubiquity of IEPOX in remote forested areas, the branching between these pathways is of primary importance to local formation of SOA and small OVOCs. The experiments in Chapter 2 were designed to determine the relative importance of the gas phase oxidation pathway. Using synthetic standards of three IEPOX isomers, chamber experiments were performed to measure the isomers' rates of reaction with

OH, oxidation products, and relative abundances from isoprene oxidation. The use of GC-CIMS to separately quantify IEPOX isomers proved crucial in determining that two isomers – *cis*- and *trans*-β – comprise nearly all IEPOX formed in the atmosphere, and that they are consistently formed in a 1:2 ratio from isoprene oxidation.

Chapter 3 continues this same line of enquiry by following the oxidative chemistry of isoprene one generation further. Three putative products of the reactions of *cis*- and *trans*-β-IEPOX with OH, proposed in Chapter 2, were synthesized and oxidized in a series of chamber experiments. 3,4-dihydroxy-2-butanone (DHBO) was identified as the major product from both IEPOX isomers, and the rates and products of its own reaction with OH were measured. The results from these experiments were then compared against field measurements and used to assemble a multigenerational mechanism of IEPOX oxidation. Global simulations with this mechanism using GEOS-Chem showed that 54 Tg of DHBO and other C_4 dihydroxycarbonyl compounds are produced annually from IEPOX – roughly a 10% overall mass yield from isoprene.

Chapter 4 focuses further on the compilation of isoprene oxidation mechanisms for modeling purposes. The IEPOX mechanism in Chapter 3 is combined with those of other isoprene oxidation pathways from numerous additional studies (including those described in Appendices B-E regarding methyl vinyl ketone, methacryloyl peroxynitrate, ISOPOOH, and isoprene ozonolysis) to create a new state-of-the-science explicit isoprene oxidation mechanism. With particular emphasis on the initial peroxy radical dynamics, oxidant budgets, and compounds known or suspected to contribute to organic aerosol formation, the explicit mechanism is presented primarily for use in box modeling, although an accompanying reduced mechanism condenses the model down to a size more manageable for chemical transport models while retaining its most salient features. Future work will then incorporate this reduced mechanism into GEOS-Chem and, in a series of global simulations, examine its effects on oxidant budgets, aerosol precursors, and small OVOCs of interest. Preliminary results show that the updated mechanism enhances NO_x transport and reduces ozone formation compared to previous parameterizations, and substantially improves the model's ability to accurately capture the relative importance of each isoprene peroxy radical isomer and its subsequent chemistry.

Chapter 5 addresses another atmospheric fate of IEPOX: reactive uptake onto particles and formation of SOA. Using the same synthetic IEPOX isomers from

Chapter 2, additional chamber experiments were performed to examine the uptake of IEPOX onto seed aerosol composed of various inorganic salts with a range of particle liquid water contents. IEPOX was found to undergo kinetically limited partitioning onto hydrated ammonium sulfate and, to a lesser extent, ammonium chloride seeds, but not onto dry seeds or those with other cations, suggesting a role for ammonium in the reactive uptake of IEPOX into aqueous aerosol. The Henry's Law constants of *cis*- and *trans*-β-IEPOX were also measured, and the organic aerosol growth from the two isomers was not found to differ significantly.

Finally, Chapter 6 concludes with a brief summary of the atmospheric fate of IEPOX, the significance of the HO_2-dominated isoprene oxidation pathway, and directions for further research.