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Atmospheric Chemistry of Isoprene Hydroxyhydroperoxides

A DISSERTATION PRESENTED

BY

JEAN C. RIVERA RIOS

TO

THE DEPARTMENT OF CHEMISTRY AND CHEMICAL BIOLOGY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

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Atmospheric Chemistry of Isoprene Hydroxyhydroperoxides

ABSTRACT

Atmospheric oxidation of volatile organic compounds (VOCs) leads to the formation of ozone (O_3) and secondary organic aerosol (SOA), known atmospheric pollutants. These compounds have been shown to have negative health effects and in the case of SOA, have significant impacts on radiative forcing. Understanding the mechanisms of the atmospheric oxidation of VOCs helps improve models and allows us to predict their effects on air quality. VOCs are emitted by both anthropogenic and biogenic sources. Isoprene dominates biogenic emissions on a global scale making isoprene oxidation a significant topic in atmospheric chemistry. Despite considerable research efforts, the oxidation of isoprene in remote locations, which represents a large fraction of emitted isoprene, is not well understood.

Oxidation of isoprene in remote environments leads to the formation of organic hydroperoxides known as isoprene hydroxyhydroperoxides (ISOPOOH). Due to a lack of synthetic standards, the atmospheric oxidation of organic hydroperoxides in general has only been studied indirectly, e.g., during oxidation experiments starting with isoprene. In this work, we synthesize standards of the most important ISOPOOH isomers and study their fate in the atmosphere.

Our work covers three topics: 1) Characterization of instrumentation commonly used for ambi-

ent VOC measurements. We find that ISOPOOH can interfere with measurements of methyl vinyl ketone and methacrolein, products of isoprene oxidation in anthropogenically influenced environments. 2) We study the role of ISOPOOH during in-cloud oxidation and show that ISOPOOH oxidation in clouds leads to SOA formation with distinct characteristics. 3) We investigate the gas-phase isoprene oxidation mechanism and its products using a combination of chamber experiments and modeling using the Master Chemical Mechanism. We suggest changes that improve the representation of isoprene oxidation under a variety of atmospheric conditions.

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TO MY MOTHER, THANK YOU FOR CARING.

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Introduction

The atmosphere refers to the envelope of gases that surrounds planet Earth. It is composed primarily of nitrogen, oxygen and argon with other gases contributing to a smaller extent. The atmosphere is essential to life on our planet. It provides the oxygen and nitrogen that is used by most organisms to extract and store energy. It also shields our planet from the harshest radiation that is emitted by the sun. The interactions of the atmosphere with the planet's rotation and solar energy gives rise to wind, precipitation and other weather events.

Although the atmosphere is composed of freely flowing gases, it can be divided into layers. These layers extend from the surface of the planet into space. Pressure decreases exponentially with elevation. However, temperature initially decreases with height, a behavior that reverses at several points. These points mark the boundaries between each layer of the atmosphere. From the bottom up these

layers are called: troposphere, stratosphere, mesosphere and ionosphere. The lowest layer extends from the surface to about 6-12 km. This height depends on the strength of convection and is usually the highest at the tropics. The stratosphere is above the troposphere and contains the ozone layer. Almost all human activities occur in the two layers closest to the surface. The mesosphere and higher layers contain gases at very low pressures that interact with the most energetic radiation from the sun and space.

Atmospheric chemistry is the study of chemical processes that take place in the atmosphere. It is an inherently multidisciplinary field. Inorganic gas-phase chemistry powers radical cycles that make the atmosphere an oxidative environment. The compounds that are oxidized are often organic in nature and their oxidation mechanisms belong to physical organic chemistry. State of the art analytical techniques are needed in order to detect chemical species in the atmosphere whose concentrations are often below parts per million. Developing and constructing new instrumentation requires significant engineering efforts. Finally, collecting, analyzing, storing and modeling data from atmospheric experiments and field campaigns requires significant inputs from computer science and engineering.

The study of the chemistry of our atmosphere comes from a place of need. Inadequate understanding of human interactions with our atmosphere has led to environmental catastrophes like the London Smog.⁶³ There, soot and sulfur dioxide emissions combined with mist and stagnant weather led to the deaths of 13,000 people. More recently, photochemical smog became a trademark of big metropolitan areas like Los Angeles for decades.⁴² Environmental regulation based on scientific understanding of the processes that lead to smog has resulted in a steady decline of pollution events. However, in cities in developing countries like India and China, smog continues to pose a threat to human health. Epidemiological studies have shown that air pollution is dangerous to humans, leading to millions of deaths every year.^{29,78}

Another example of the need for atmospheric chemistry is the depletion of ozone in stratosphere, known as the ozone hole. Emissions of chlorofluorocarbons, compounds found to be safe and gen-

erally unreactive, were shown to be the cause of the loss of ozone particularly over polar regions. Their low reactivity allowed them to be transported high into the atmosphere, where ultraviolet radiation breaks carbon-halogen bonds. These halogens then proceed to destroy ozone in a catalytic manner. A combination of laboratory experiments, field campaigns and extensive modeling led to: the use of alternative compounds, the adoption of the Montreal Protocol in 1987 and the Nobel Prize in chemistry for Crutzen, Molina and Rowland in 1995. This remains one of the best examples of science driven policy. Recent measurements show a recovery in the ozone layer, impossible without the efforts of atmospheric scientists.⁹⁸

Despite the successes of our field, air pollution continues to be an issue in many places around the world. In the USA, the Environmental Protection Agency (EPA) has improved air quality by enforcing the Clean Air Act.⁸⁸ These regulations limit the emissions of criteria pollutants like sulfur dioxide (SO₂) from power plants as well as emissions of nitrogen oxides from vehicle exhausts and power plants. The suggested concentrations for regulated species are known as the National Ambient Air Quality Standards (NAAQS). The monitored compounds are SO₂, particulate matter smaller than 10 μm in diameter (PM₁₀), fine particulate matter (smaller than 2.5 μm, PM_{2.5}), carbon monoxide, ozone and lead. SO₂ comes primarily from coal power plants that burn fuel containing sulfur impurities. Lead and CO are products of combustion engines used in vehicles. The ban on leaded gasoline has reduced ambient lead levels to acceptable levels. Ozone and particulate matter have complex behaviors and are products of photochemical oxidation of volatile organic compounds (VOCs). Their regulation requires a good understanding of VOC emissions, oxidation pathways and production and enhancements of particles known as secondary organic aerosols.

VOCs are carbon containing compounds emitted into the atmosphere by a variety of sources. Human activities like oil extraction,¹ and transportation⁴³ lead to the release of anthropogenic VOCs like alkanes and aromatic compounds. Vegetation is another source of VOCs and globally it is by far the largest contributor. VOCs emitted by plants are called biogenic (BVOC). Isoprene⁴¹

is the main compound emitted by plants with monoterpenes like α -pinene having a smaller but significant contribution.¹ Oxidation leads to functionalization of the VOCs which has significant impacts on the properties of these compounds. Addition of functional groups can allow otherwise volatile species to partition into aerosols or undergo reactions leading to their uptake.

The work presented in this thesis focuses on understanding the oxidation of isoprene. Isoprene is emitted into the atmosphere by deciduous trees in very large amounts (500 Tg yr^{-1}). Its emission is correlated with sunlight and temperature with emissions peaking during the day in summertime. In the United States, emissions of isoprene are largely concentrated in the southeast. Large emissions, coupled with high reactivity make the atmospheric oxidation of isoprene vital to understanding atmospheric photochemical processes in forested regions. Although the chemistry of isoprene has been studied for many years, significant gaps remain in our understanding of processes that control everything from emissions,⁴¹ oxidation,¹⁰⁴ secondary organic aerosol formation¹¹ and more.

Atmospheric oxidation is a complex process.³ To understand isoprene oxidation it may be useful to understand the oxidation of a simpler compound: methane. Figure 2 shows how methane is oxidized by the OH radical. Oxidation begins when the hydroxyl radical abstracts a hydrogen from the methane molecule. This leads to an alkyl radical (CH_3) that quickly reacts with oxygen to form a peroxy radical (CH_3O_2). The fate of this peroxy radical depends on the concentrations of hydroperoxyl (HO_2) and nitric oxide (NO). Nitrogen oxides (NO_x) which include nitric oxide, nitrogen dioxide and the nitrate radical (NO_3) are emitted as a result of human activities, in particular transportation. For this reason, oxidation pathways that involve NO_x are commonly associated with modern or urban conditions. Under pre-industrial conditions anthropogenic sources of NO_x were limited (lightning and soil bacteria are natural sources) and HO_2 played a bigger role in the fate of RO_2 radicals. However, HO_2 still plays a significant role in areas that are remote or “pristine” environments like the Amazon rainforest.

Reaction of CH_3O_2 with NO leads to NO_2 and an alkoxy radical (CH_3O) that quickly reacts

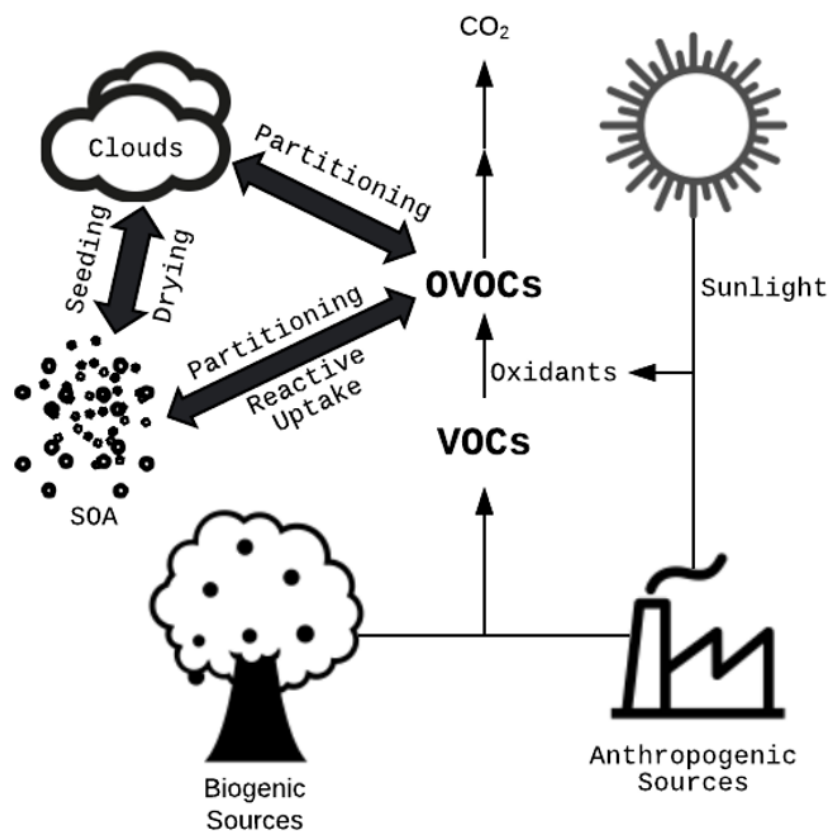


Figure 1: Sunlight sustains the radical cycles that make the atmosphere an oxidative environment. VOCs are emitted from biogenic and anthropogenic sources. Oxidants, which include the hydroxyl radical and ozone, oxidize the emitted VOCs into oxygenated volatile organic compounds (OVOCs). The oxidation process introduces oxygen containing functional groups that can significantly change the compounds reactivity and volatility. OVOCs can then continue to be oxidized in the gas phase and/or partition into particles or clouds. OVOCs are eventually oxidized completely into CO₂ or removed from the atmosphere by deposition.

with oxygen forming formaldehyde and HO_2 . Formation of carbonyl compounds is typical of high NO_x oxidation. Although relatively unimportant for methane, reaction of RO_2 with NO can also lead to organic nitrates (RONO_2). This chain terminating reaction can lead to species that can act as NO_x reservoirs and can be a sink for NO_x depending on the structure of the resulting organic nitrate. High NO_x oxidation conditions are self-sustaining if there is enough sunlight. NO_2 is photolysed leading to NO and an oxygen atom which can lead to O_3 formation. NO can react with HO_2 to produce NO_2 and OH , which can continue the oxidation cycle. O_3 photolysis leads to molecular and atomic oxygen, the latter's reaction with water leads to OH as well. Conditions high in NO_x and volatile organic compounds can lead to large amounts of O_3 production, directly affecting human health and the environment. The effects of NO_x and VOC concentrations on ozone production are non-linear with NO_x concentrations promoting O_3 production at low concentrations and depleting O_3 and OH at high concentrations.

Reaction of the same peroxy radical (CH_3O_2) with HO_2 can lead to methyl hydroperoxide (CH_3OOH). Formation of hydroperoxides is a chain terminating reaction. This peroxide can react with OH leading to formaldehyde and recycling OH . Recycling of OH by hydroperoxides is an important contributor to OH levels in remote locations. Unfortunately, due to a lack of commercial standards, the study of atmospherically relevant organic hydroperoxides has been limited to simple compounds like alkyl hydroperoxides. Detection of hydroperoxides at the levels found in the atmosphere is also a challenging problem. Their oxygen-oxygen bond is relatively weak and can break during analysis leading to misidentification as shown in chapter 1.

Methane and isoprene are oxidized by the same mechanisms. A large amount of scientific effort has been invested in understanding isoprene oxidation.¹⁰⁴ A number of chamber experiments and field campaigns have been designed around studying the fate of isoprene under a variety of conditions. A simplified mechanism of the first step of isoprene oxidation is shown in figure 3. Isoprene has 5 carbons. OH reacts with isoprene's double bonds by addition leading to an alcohol radical.

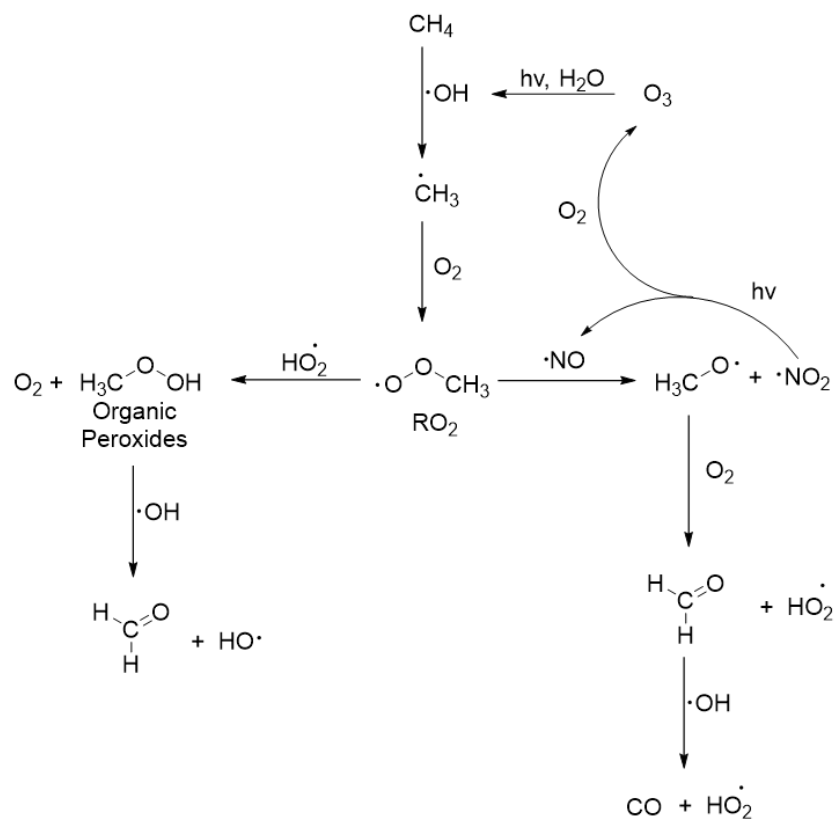


Figure 2: Oxidation scheme for methane. Hydrogen abstraction by OH creates a methyl radical that quickly reacts with oxygen leading to a methylperoxy radical ($\text{CH}_3\text{OO}\cdot$). The fate of this peroxy radical depends on the concentrations of HO_2 and NO which lead to hydroperoxides and carbonyl products respectively. Oxidation of the peroxide leads to formaldehyde in an additional step that recycles OH. Formaldehyde undergoes photolysis or reaction with OH to form CO. The lifetime of CO is 1-3 months while that of methane is 8.4 to 12 years. Formaldehyde has a shorter lifetime, usually a few hours.

This radical reacts quickly with oxygen leading to an RO₂ radical, as is the case for methane. Hydroxyl adds primarily to the 1 and 4 carbons. Addition to these carbons leads to an allylic radical which is significantly more stable than the primary radicals formed from addition to the 2 and 3 carbons. Since the main radicals are allylic, oxygen addition can proceed at the β and δ positions leading to 6 total peroxy radicals (when considering cis trans isomerism). The RO₂s generated from isoprene oxidation are significantly more complex than the methane RO₂ and have additional reaction pathways. However, their fates are also controlled by NO_x and HO₂ levels.¹⁰¹ The topic of this thesis are the products of isoprene RO₂ with HO₂: isoprene hydroxy hydroperoxides.

Isoprene hydroxy hydroperoxides (ISOPOOH) are the main products of isoprene low NO_x oxidation. Approximately 180 Tg of ISOPOOH are formed each year. Before this work, their study was limited to oxidation experiments starting with isoprene. ISOPOOH oxidation has been shown to lead to IEPOX, an epoxide, while recycling OH.⁸¹ IEPOX has been studied extensively since it undergoes reactive uptake in the presence of acidic aerosol.¹⁴ In this work we synthesize isoprene hydroxyhydroperoxide standards. We then use these standards to evaluate their role in atmospheric chemistry. The first chapter focuses on how we measure these peroxides in the atmosphere and challenges that were found in typical instrumentation. The second chapter evaluates the chemistry of ISOPOOH when it partitions into atmospheric waters, like clouds, and oxidation takes place in that environment. Finally, in a third chapter we evaluate isoprene's oxidation mechanism as represented in the Leeds Master Chemical Mechanism (MCM), including experiments starting with ISOPOOH and IEPOX and try to build a self-consistent mechanism that works under a variety of NO_x conditions.

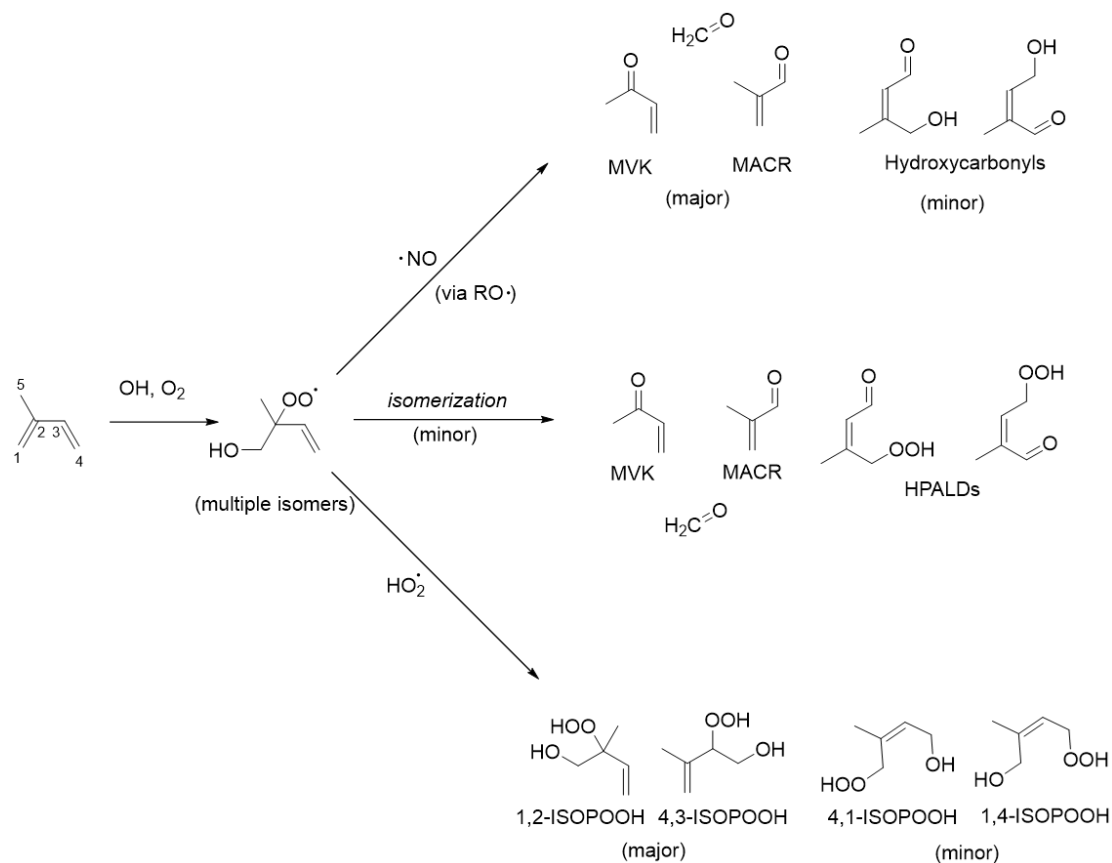


Figure 3: Simplified oxidation scheme for isoprene. Oxidation under high NO_x conditions leads to Methacrolein (MACR) and methyl vinyl ketone (MVK) along with formaldehyde (HCHO). High NO_x products of the β O₂ addition are C5 hydroxy carbonyls. Isomerization of the RO₂ compounds can lead to hydroperoxy aldehydes or to MACR, MVK and HCHO. The work presented in this thesis focuses on the major ISOPROOH isomers (1,2-ISOPROOH and 4,3-ISOPROOH).

1

Conversion of hydroperoxides to carbonyls
in field and laboratory instrumentation:

observational bias in diagnosing pristine
versus anthropogenically-controlled
atmospheric chemistry

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They have been adapted to match the format of this dissertation.

I.I ABSTRACT

ATMOSPHERIC VOLATILE ORGANIC COMPOUND (VOC) oxidation mechanisms under pristine (rural/remote) and urban (anthropogenically-influenced) conditions follow distinct pathways due to large differences in nitrogen oxide (NO_x) concentrations. These two pathways lead to products that have different chemical and physical properties and reactivity. Under pristine conditions, isoprene hydroxy hydroperoxides (ISOPOOHs) are the dominant first-generation isoprene oxidation products. Utilizing authentic ISOPOOH standards, we demonstrate that two of the most commonly used methods of measuring VOC oxidation products (i.e., gas chromatography and proton transfer reaction mass spectrometry) observe these hydroperoxides as their equivalent high-NO isoprene oxidation products – methyl vinyl ketone (MVK) and methacrolein (MACR). This interference has led to an observational bias affecting our understanding of global atmospheric processes. Considering these artifacts will help close the gap on discrepancies regarding the identity and fate of reactive organic carbon, revise our understanding of surface-atmosphere exchange of reactive carbon and SOA formation, and improve our understanding of atmospheric oxidative capacity.

1.2 INTRODUCTION

Atmospheric oxidation of volatile organic compounds (VOCs) is driven by catalytic cycles of hydrogen oxides ($\text{HO}_X = \text{OH} + \text{HO}_2$) and nitrogen oxides ($\text{NO}_X = \text{NO} + \text{NO}_2$). These oxidation reactions are coupled to the formation of secondary pollutants, e.g., ozone and secondary organic aerosol (SOA), which affect climate, human health and the environment. VOC reactivity can also impact the atmospheric oxidative capacity, which is dominated by the OH radical, thereby controlling the lifetime of many atmospheric trace constituents, including important greenhouse gases such as methane and hydro(chloro)fluorocarbons. This work focuses on isoprene, the predominant biogenic emission from vegetation which contributes about one third of global non-methane VOC emissions (i.e., reactive carbon).⁴¹ The peroxy radical (RO_2) formed in the first step of (O)VOC oxidation (OVOC = oxidized VOC) primarily reacts with either HO_2 or with NO (fig.1.1), the latter of which is largely anthropogenic in origin. Reactions with HO_2 dominate the fate of RO_2 under pristine conditions.²¹ The pristine reaction products of isoprene, i.e., the hydroxy hydroperoxides (ISOPOOHs) have very different chemical and physical properties than their urban counterparts. The pathways have different radical chain propagation properties, which directly impacts secondary pollutant production and oxidative capacity.²⁰ Modeling work demonstrates that only 30% of isoprene RO_2 reacts with NO globally, highlighting the importance of pristine products.²¹ In the Western and Southeastern United States, ISOPOOH concentrations over one part-per-billion (ppb)¹⁰⁷ have been observed with the Caltech CF_3O^- triple-quadrupole chemical ionization mass spectrometer (CIT-3Q-MS),^{81,94} rivaling concentrations of urban products. Due to regulations on NO_X emission, most of the US, including the Southeast, is experiencing decreasing NO_X concentrations.⁸⁷ As a result, pristine products are increasing in importance. Accurate understanding of the chemistry and contribution of pristine VOC oxidation products is central to the capabilities of models to predict secondary pollutant concentrations, oxidative capacity, and the role of anthropogenic

influence. Accurate atmospheric model results are particularly important for making informed regulatory decisions.

We describe here work that uses synthesized standards of the two main isomers of ISOPOOH, the dominant hydroperoxides derived from non-methane VOCs, for detailed characterization of the most widely used instrumentation for monitoring VOC oxidation products: gas chromatography (GC) and proton-transfer-reaction mass spectrometry (PTR-MS). We find that the peroxy bond in ISOPOOH is sufficiently weak that fragmentation is facile leading to misidentification of ISOPOOH.

1.3 EXPERIMENTAL

Characterization of ISOPOOH isomers and instrument details are described in the additional information section. At Caltech, we introduced 1,2 and 4,3-ISOPOOH standards (see figures 1.6 and 1.7 for structures) into an Agilent 6890N commercial GC with flame ionization detector (GC-FID). The resulting chromatograms included signals at the elution times of MVK and MACR, respectively (Figure 1.2). The conversion rates for both isomers are greater than 70%. The observation was reproduced with the NOAA GC-MS field instrument under standard field operating conditions (Figure 1.8). The mass to charge ratios (m/z) in the GC-MS were consistent with those from MVK/MACR standards. The results show that ISOPOOH is detected with significant conversion efficiency as MVK and MACR in GC instrumentation used in both laboratory and field studies.

While sampling with the (quadrupole) PTR-MS (Ionicon Analytik), 1,2-ISOPOOH was detected as a product ion with m/z 71, consistent with $C_4H_7O^+$ (MVK/MACR) with an efficiency of 44% (+21/-12%) of the sensitivity of MVK based on the 1,2-ISOPOOH mixing ratio determined with the CIT-ToF-MS (California Institute of Technology Time of Flight Mass Spectrometer). Both ISOPOOH isomers produced significant $C_4H_7O^+$ (m/z 71.050) signals in the H_3O^+ mode

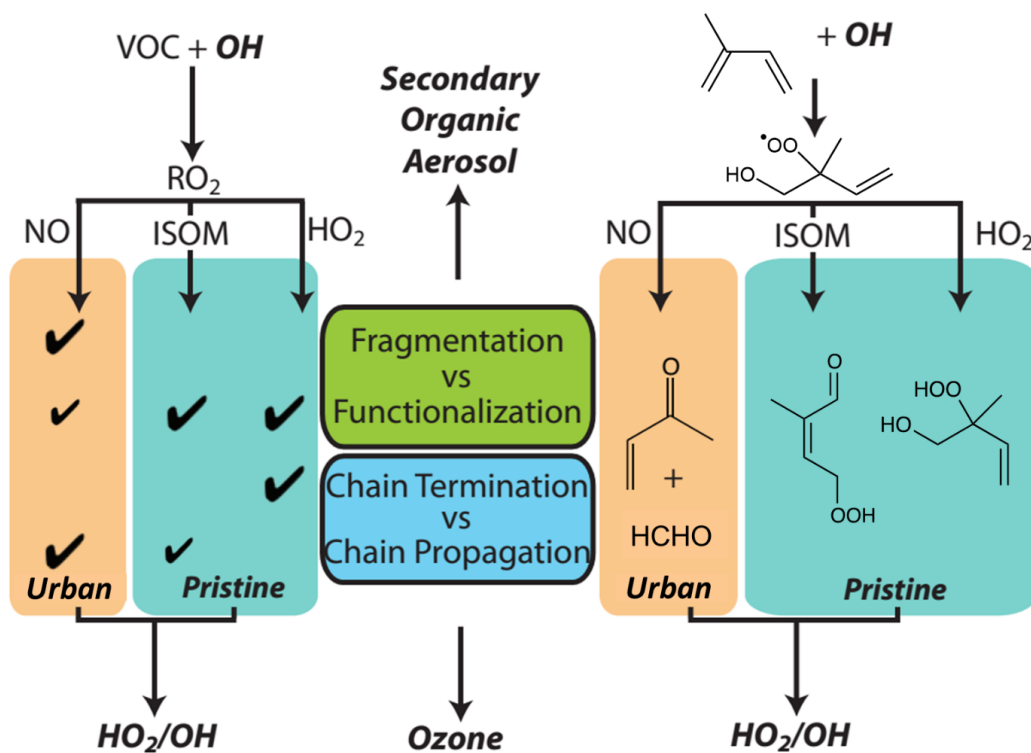


Figure 1.1: (Left) General VOC oxidation scheme under urban and pristine conditions. Reaction of peroxy radicals (RO_2) with NO under urban conditions results in different first-generation oxidation products than reaction with HO_2 or unimolecular isomerization (ISOM), which dominate under pristine conditions and are important even under intermediate conditions. (Right) OH radicals react with isoprene to form hydroxy-peroxy radicals (RO_2). Differences in chemical and physical properties of products, e.g., the degree of functionalization and fragmentation, impacts SOA formation potential. Differences in the degree of radical propagation impacts ozone formation and oxidative capacity.

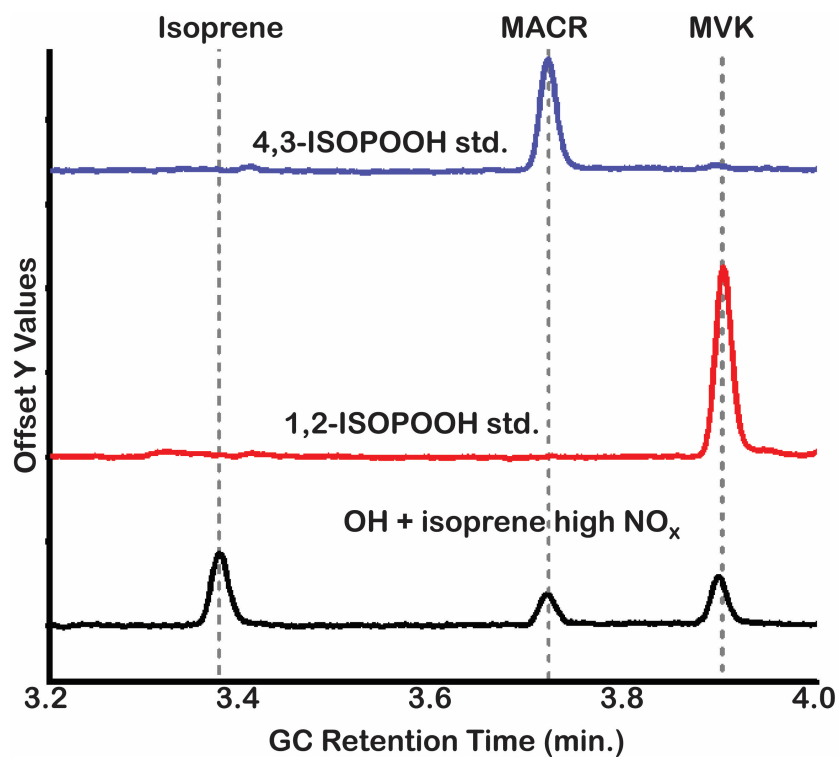


Figure 1.2: The bottom gas-chromatogram from an isoprene oxidation experiment under high-NO_x (urban) conditions shows the characteristic elution times of isoprene, MACR and MVK, sampled through 3 feet 1/8" OD PFA Teflon tube submerged in a -40 °C cold trap to remove lower-volatility contaminants that would interfere with authentic MACR and MVK determinations.⁷¹ The middle (red) and top (blue) traces are from experiments without the cold trap in which authentic 1,2-ISOPROOH and 4,3-ISOPROOH standards were introduced, respectively. Conversion yields of greater than 70% were obtained for the ISOPROOH isomers demonstrating that pristine products are detected as their urban counterparts.

of the switchable reagent ionization time-of-flight MS (SRI-ToF-MS, University of Innsbruck). Using NO^+ as reagent ion confirmed that $\text{C}_4\text{H}_7\text{O}^+$ observed from 1,2 and 4,3-ISOPPOOH correspond to MVK and MACR, respectively. The results with NO^+ also unambiguously demonstrate the fact that the decomposition of ISOPPOOH occurs before any interactions with the reagent ions. These results are consistent with a recent study that observed MACR/MVK ($\text{C}_4\text{H}_7\text{O}^+$) in low- NO_x isoprene oxidation experiments.⁷¹ The authors proposed that the observed signal is an analytical interference by ISOPPOOH, but could not prove this due to lack of standards. Our work unambiguously confirms that ISOPPOOH results in this interference in PTR-MS and SRI-ToF-MS, but does not rule out other products as precursors to the $\text{C}_4\text{H}_7\text{O}^+$ signal.

Overall, experiments demonstrate that in both GC and PTR instrumentation, 1,2- and 4,3-ISOPPOOH are detected with high conversion efficiency as MVK and MACR, respectively. Although whole air sampling methods were not tested, it is likely that these are also impacted by ISOPPOOH decomposition upon sampling. Previous instrument intercomparisons of PTR-MS, online GC and whole air samples with offline GC analysis may not be aware of the analytical challenges posed by ISOPPOOH,^{26,25} possibly because the interference has a common effect among these methods.

1.4 INTERFERENCE MECHANISM

Knowledge of the interference mechanism can guide experimental advances that allow distinct detection of ISOPPOOH and MVK/MACR. Mechanistic understanding is also required to assess the implications beyond ISOPPOOH-MVK/MACR. Organic hydroperoxides are inherently unstable species and are susceptible to a variety of decomposition mechanisms. A common reaction is homolytic cleavage of the weak peroxy bond (O-OH). This reaction can be catalyzed by metals.^{33,103,15} Based on our work, we propose that the initial step of the ISOPPOOH decomposition occurs via

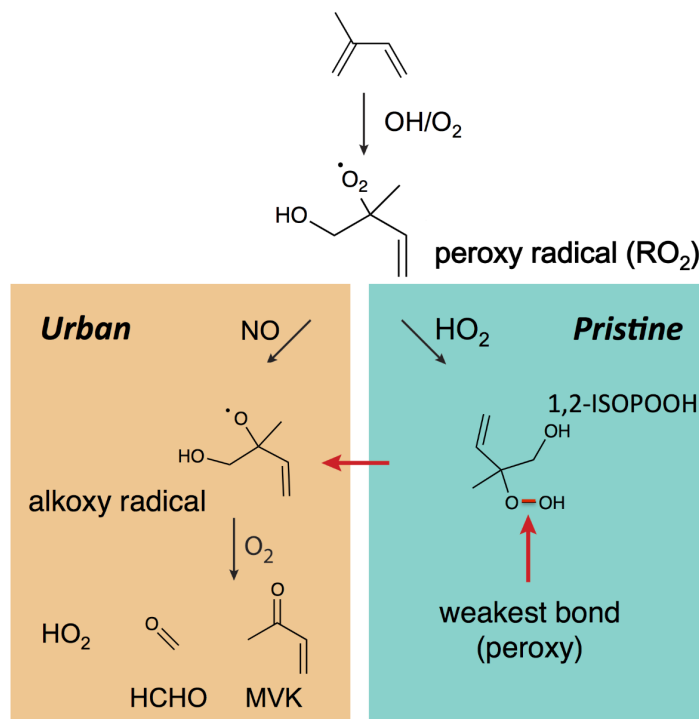


Figure 1.3: Proposed interference mechanism: Under high NO_x conditions peroxy radicals react with NO to form alkoxy radicals that fragment rapidly to form carbonyls, e.g., MVK and formaldehyde, and the hydroperoxy radical (HO₂), which is recycled to OH via reaction with NO. Reaction of the peroxy radical with HO₂ under pristine conditions forms a hydroperoxide. Breaking of the O-O bond, the weakest molecular bond, produces the alkoxy radical that is formed under urban (high NO_x) conditions.

homolytic peroxy bond cleavage on metal surfaces in the GC and PTR-MS instrumentation (Figure 1.3 and 1.8). This produces the isomer-specific alkoxy radicals, analogous to those formed under high NO_x conditions in the gas phase, which immediately decompose to MVK and MACR, and formaldehyde. This suggestion rationalizes the production of MVK from 1,2-ISOPROOH and MACR from 4,3-ISOPROOH.

These findings highlight that our observationally-based understanding of VOC oxidation in the atmosphere may be influenced by an observational bias toward the urban, high NO products.

The source of this bias was not diagnosed previously due to a lack of standards of pristine oxidation products, which has prevented fundamental mechanistic studies of their physical and chemical properties.⁷¹ In addition, there have been few ambient observations of these compounds^{81,107} resulting from a combination of limitations in instrumentation to specifically observe these products and no standards to calibrate and characterize instrument performance.

1.5 IMPLICATIONS

The chemical and physical properties of the pristine products are very different from those of the urban products. Due to the aforementioned observational bias, important aspects of our understanding of tropospheric chemistry may need to be revisited, in particular, those involving the budget and surface-atmosphere exchange of reactive carbon, oxidative capacity and SOA formation. First, we discuss the implications arising from the difference in physical and chemical properties of ISOPOOH and MVK/MACR and then the broader context. It should be noted that the extent of this interference depends on the conversion efficiency, as stated in the previous section.

After initial attack of the OH radical, reaction of the resulting RO₂ radical with HO₂ to form ISOPOOH retains the C5 carbon backbone, i.e., there is no fragmentation, and the oxygen to carbon (O:C) ratio is higher than for the C4 fragmentation products from the reaction of RO₂ with NO (fig. 1.4)^{51,52,90}. Furthermore, ISOPOOH contains polar alcohol and hydroperoxide functional groups that are capable of strong hydrogen bonding. The greater polarity and mass of ISOPOOH explains why its vapor pressure is more than three orders of magnitude lower than that of MVK and MACR, calculated using SIMPOL⁸⁰. Thus, partitioning to surfaces and the condensed phase, e.g., dry and wet deposition, is much more important for ISOPOOH than MVK/MACR.

Studies using PTR-(ToF)-MS have highlighted unexpectedly high deposition fluxes of VOC oxidation products, in particular of MVK/MACR, in pristine conditions that are expected to

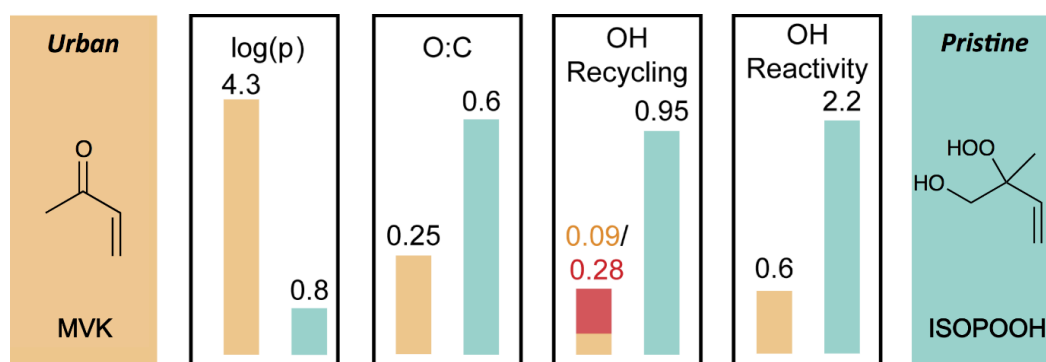


Figure 1.4: Urban (orange and red, represented by MVK) and pristine oxidation products (green, represented by 1,2-ISOPOOH) have important differences in their chemical and physical properties. The vapor pressure ($\log(p)$) of MVK/MACR is much smaller than that of ISOPOOH due to differences in functional groups (carbonyl in MVK/MACR, alcohol and hydroperoxide for ISOPOOH) and due to the fact that ISOPOOH has a higher number of carbons since the isoprene carbon skeleton does not fragment in the first steps of the pristine oxidation pathway. The oxygen to carbon ratio (O:C) of ISOPOOH is also much higher since the hydroperoxide group contributes two extra oxygen atoms when compared to MVK/MACR. Under pristine conditions, reaction of OH with ISOPOOH returns OH efficiently after formation of IEPOX. Direct recycling of OH is much lower for the urban products since it depends on significantly slower 1,4 or 1,5 hydrogen shifts. Finally, for a given OVOC concentration, the OH reactivity (s^{-1}) of ISOPOOH is much higher than that of MVK/MACR due to the difference in their OH reaction rate constants. The values shown in this figure are for the isomeric mixture but, for simplicity, only MVK and 1,2-ISOPOOH are shown (see additional information)

be influenced by high ISOPOOH concentrations^{57,75}. Although it is unclear how much, if any, ISOPOOH contributed to the observed signals at the m/z of MVK/MACR, larger than expected deposition fluxes are consistent with a non-negligible interference. Overall, the interference mechanism suggests that surface-atmosphere exchange of reactive carbon should generally be revisited with respect to the identity and O:C ratio of reaction products.

For ISOPOOH, reactive partitioning to aerosol needs to be considered, whereas it is unimportant for MVK/MACR. The functional groups of ISOPOOH allow numerous condensed phase reactions, such as esterification, breaking of the peroxy bond, and addition to the double bond. The lower vapor pressure and the largely unexplored, but likely high condensed-phase reactivity of ISOPOOH make it a potential SOA precursor via reactive uptake. Further, in contrast to MVK and MACR, ISOPOOH is an SOA precursor via formation of isoprene epoxydiols, which have half the vapor pressure of ISOPOOH as calculated with SIMPOL, and which have been shown to form SOA via reactive uptake.⁷⁷ Observations of MVK and MACR have also been used to estimate OH concentrations.^{56,62} For an observed compound with concentration [OBS] the observed or inferred loss rate from reaction with OH is given by:

$$\frac{d[OBS]}{dt} = -k_{OBS+OH}[OBS][OH]$$

where k_{OBS+OH} is the reaction rate of the observed compound and [OH] the OH radical concentration. For an observed OVOC loss rate, OH will be a factor of 3.75 lower if the observed compound is ISOPOOH compared to MVK/MACR due to the difference in k_{OBS+OH}

The implications for studies that use OVOC/isoprene ratios to infer [OH] are complicated due to the fact that the reaction rate of ISOPOOH is much closer to that of isoprene than that of MVK/MACR and, importantly, the isoprene oxidation yields of MVK/MACR and ISOPOOH are significantly different. In addition, the conversion efficiency, which can vary between instru-

ments, has to be considered. Figure 1.9 shows a study in which the vertical profile of these ratios is modeled following the method of Karl.⁵⁶ Clearly, OH concentrations inferred by this method will depend on the identity of the observed compound. Hence conclusions drawn on oxidative capacity from MVK/MACR observations have to be carefully reconsidered. Finally, studies that have used MVK/MACR to infer details about reaction mechanisms³⁴ need to be revisited as MVK/MACR and ISOPOOH are formed by different mechanisms.

The implications for radical chain propagation are complex. The formation of ISOPOOH from isoprene is a much stronger HO_x sink than the formation of MVK/MACR. ISOPOOH formation is radical chain terminating, as it converts one molecule of OH, isoprene and HO₂ into one molecule of ISOPOOH. This will decrease OH concentrations, thereby lowering oxidative capacity. However, the net effect on the oxidative capacity also has to reflect the fact that OH is recycled during the oxidation of ISOPOOH: oxidation of ISOPOOH is OH neutral as OH is reformed via production of IEPOX.⁸¹ The reaction to form MVK and MACR is HO_x neutral, as OH is consumed and HO₂ is formed, but according to current mechanisms HO₂ is not recycled efficiently to OH at low NO concentrations. Figure 1.4 shows the difference in OH recycling efficiency of the urban and pristine products at low NO concentrations based on the MCM v3.2 but also using the OH recycling of MACR recently described by Crounse¹⁸ shown in red. The overall effect of the difference in reactivity between ISOPOOH and MVK/MACR on HO_x is highly dependent on conditions. However, this effect is important to consider because oxidative capacity is directly related to the rate of oxidative processing, which in turn influences the rate of particle nucleation, the rate of SOA formation and, outside of low-NO_x regimes, ozone production.

The large difference in gas-phase chemical reactivity between the pristine and urban reaction products has implications for our understanding of the reactive carbon budget, rate at which reactive carbon is being processed, and the role of VOC oxidation in radical cycling. There have been extensive efforts investigating sources of reactive carbon that are currently eluding measurements,

often referred to as “missing reactivity”. Evidence for these missing VOCs comes from considerations of the overall reactive carbon budget³⁹ as well as measurements of the total sink strength of the OH radical (OH reactivity).²⁷ In regions with high biogenic emissions, the measured OH reactivity is often much higher than the reactivity calculated from the sum of measured or modeled compounds.³⁰ The missing OH reactivity corresponds to missing VOC emissions or missing reaction products. The average rate constant for reaction of OH with ISOPOOH isomers is 3.75 times that of the reaction of OH with MVK and MACR based on the MCM v3.2,^{51,52,90} see section 1.6.8. This affects the rate of carbon processing, as shown later, but it is also worth considering the effect of the interference on missing reactivity. Mistaking ISOPOOH for MVK/MACR causes an underestimation of the true OH reactivity. This is due to the fact that the OH loss rate is much higher for ISOPOOH than for MVK/MACR. However, the reaction of OH with ISOPOOH recycles OH rapidly with high yield,⁸¹ which makes it OH neutral. Despite the fast reaction rate constant of ISOPOOH, an OH neutral reaction will not be reflected in the measured OH reactivity since it does not deplete OH. Therefore, care has to be taken when comparing modeled and measured OH reactivity if the modeled OH reactivity includes the loss of OH to reaction with ISOPOOH. The fact that the measured OH reactivity does not reflect ISOPOOH, suggests that if ISOPOOH is mistaken for MVK/MACR the calculated OH reactivity will be overestimated.

The interference also affects estimates of the amount of reactive carbon being oxidized. For a given production rate of isoprene-RO₂, as determined by isoprene emissions and oxidative capacity, the steady-state concentration of ISOPOOH will be 3.75 times lower than that of MVK/MACR, due to the shorter lifetime of ISOPOOH with respect to OH. The net carbon flow through first generation oxidation products under this scenario remains identical. Alternatively, if ISOPOOH and MVK/MACR mixing ratios are the same, a steady-state scenario implies a much higher carbon-processing rate for ISOPOOH than for MVK/MACR. Hence, if the carbon processing rate through these products is estimated on the basis of an observation that assumes MVK/MACR, but actually

corresponds to ISOPOOH, the total rate will differ by a factor of 3.75.

Globally, reaction of RO_2 is expected to be dominated by reaction with HO_2 .²¹ Although the fate of this reaction depends on the details of the specific RO_2 , large concentrations of organic hydroperoxides will be formed. The work presented here demonstrates that the observational artifact, which projects these pristine products causally onto their urban counterparts, has introduced an observational bias as urban product concentrations have likely been overestimated while pristine products have been under-represented. This effect is compounded by the fact that very few observations of hydroperoxides, in particular, the globally-important isoprene derived hydroxy hydroperoxides, have been published. In combination, this has resulted in a bias in our view of tropospheric chemistry even in regions with a moderate impact from urban NO_x emission. Figure 1.5 shows the ratio of ISOPOOH/(MVK+MACR) as a function of NO , HO_2 and OH , using a modified version of the MCM v3.2 that includes isomerization reactions as recent results suggest.²¹ This shows that even at ca. 500 ppt of NO , as much as 5-10% MVK/MACR signal may correspond to ISOPOOH, whereas under pristine conditions the signal may be dominated by ISOPOOH. The magnitude of the interference also depends on the conversion efficiency, which we have shown is high, but may depend on instrumental details and the identity of the hydroperoxide. Conditions globally will mostly be in an intermediate regime where reactions of RO_2 with both HO_2 and NO are important. Under these conditions, RO_2 formed from pristine products can react with “urban” NO and RO_2 formed from urban products with HO_2 . This implies that mechanistic studies of the mixed-regime chemistry, e.g., the products and radical propagation from reactions of urban products under pristine conditions (and vice versa), need to be pursued.

Overall, our work calls for studies of instrument characterization with other highly functionalized compounds, e.g., multifunctional isoprene epoxydiols and organic nitrates that could also decompose to form artifacts. Furthermore, careful reevaluation of conclusions drawn using previous observations is required and our work calls for renewed efforts in measurement of urban products.

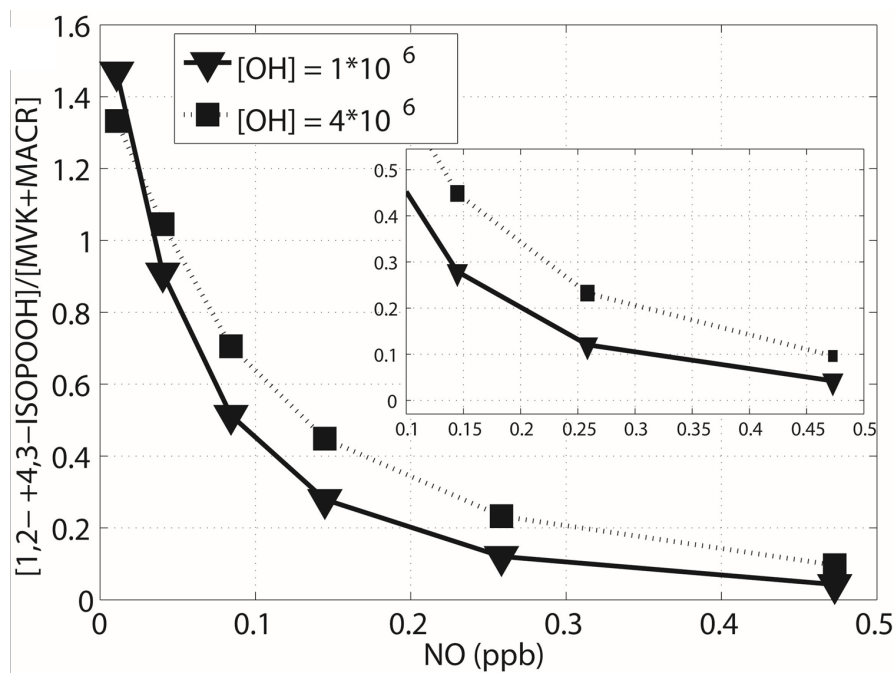


Figure 1.5: Ratio of the sum of 1,2- and 4,3-ISOPOOH to the sum of MVK+MACR as a function of OH (dashed vs solid lines), NO (x-axis) using a steady state model of isoprene (3 ppb) oxidation at a solar zenith angle of zero based on the MCM v3.2 taking into account reaction of RO₂ with NO, HO₂, RO₂ as well as isomerization. MVK+MACR at low NO arises from RO₂+RO₂ reactions under the conditions of the model run.

Reactive carbon and oxidative capacity together determine the rate of secondary pollutant production and the lifetime of greenhouse gases. The instrumental bias described here suggests that the role of pristine versus urban products should be revisited. This will improve our understanding of the fate of reactive carbon, change the view of surface-atmosphere exchange of VOC oxidation products, and may shed light on current questions of how oxidative capacity is maintained in low-NO_x environments or conditions.

1.6 ADDITIONAL INFORMATION

1.6.1 CHARACTERIZATION OF 1,2- AND 4,3-ISOPROOH

¹H and ¹³C NMR spectra were recorded on either a Bruker AV-400 or a Varian MercuryPlus 300 NMR spectrometer. Samples were quantified by preparing an NMR sample with a known amount of TMSPh, a compound that does not interfere with any of the signals from ISOPROOH.

Measurements of the synthetic standards with the Caltech triple quadrupole CF₃O⁻ CIMS instrument were consistent with previous measurements of ISOPROOH formed via low NO_x isoprene oxidation experiments, in agreement with the characterization via NMR spectroscopy. Sample degradation was tested either via CF₃O⁻ CIMS or NMR spectroscopy before experiments. Degradation of compounds was not significant when stored at -20 °C, although the compounds are susceptible to this if stored at room temperature.

1.6.2 PTR-MS STUDY

The experiment was performed using a standard quadrupole-MS based PTR-MS instrument.²⁵ This and similar instruments have been in use for MVK/MACR measurements since 1998.²² The instrument is equipped with a second-generation drift tube⁹⁶ consisting of stainless steel rings separated by Teflon PTFE spacers. The drift tube was operated at conditions typically used for field

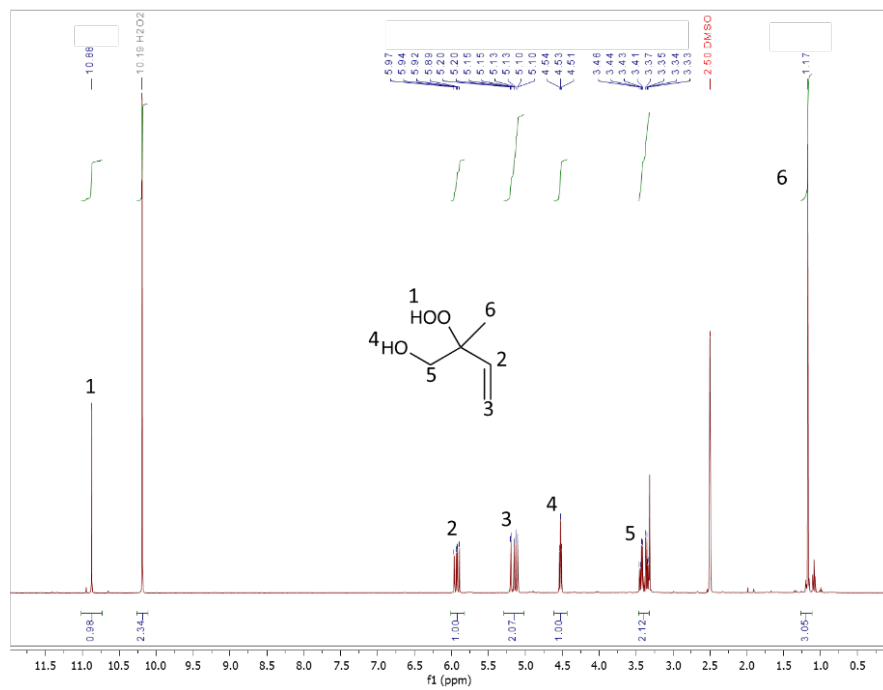


Figure 1.6: Proton NMR spectrum of 1,2-ISOPPOOH. ¹H NMR (400 MHz, DMSO-d₆) δ 10.88 (s, 1H), 5.93 (dd, J = 17.9, 11.1 Hz, 1H), 5.18 (dd, J = 17.8, 1.4 Hz, 1H), 5.12 (dd, J = 11.1, 1.4 Hz, 1H), 4.53 (t, J = 6.2 Hz, 1H), 3.43 (dd, J = 11.4, 5.9 Hz, 1H), 3.35 (dd, J = 11.5, 6.5 Hz, 1H), 1.17 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 140.36, 114.95, 83.71, 64.72, 19.01.

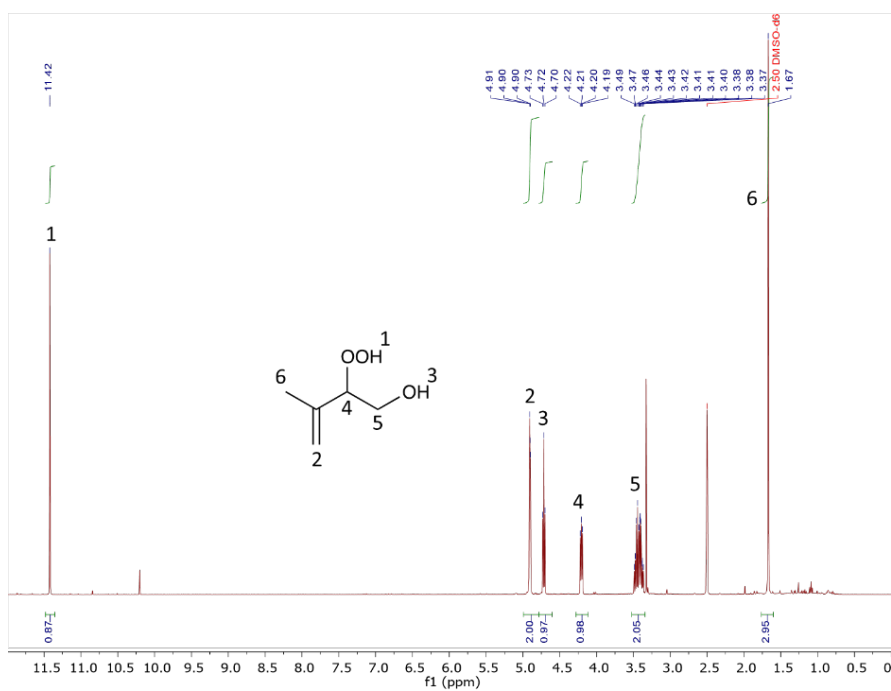


Figure 1.7: Proton NMR spectrum of 4,3-ISOPPOOH. ¹H NMR (400 MHz, DMSO-d₆) δ 11.42 (s, 1H), 4.94 – 4.83 (m, 2H), 4.72 (t, J = 5.9 Hz, 1H), 4.21 (dd, J = 6.5, 4.9 Hz, 1H), 3.52 – 3.34 (m, 2H), 1.67 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 142.91, 113.19, 89.30, 61.12, 30.68.

measurements (drift tube pressure: 2.25 mbar, drift tube voltage: 560 V, drift tube temperature: 54 °C). Inlet tubing to the drift tube exclusively consisted of Teflon PFA and PEEK. Liquid 1,2-ISOPPOOH was injected into dry synthetic air in a 0.78 m³ Teflon-FEP bag. While sampling from the bag, the PTR-MS instrument performed full mass scans in the m/z 20 to m/z 150 range to obtain the mass spectrum of 1,2-ISOPPOOH. The 1,2-ISOPPOOH concentration in the bag was 46.7 ppbV (accuracy: $\pm$ 25%) as simultaneously determined by the CIT-ToF-CIMS instrument.

1.6.3 SRI-ToF-MS STUDIES

The SRI-ToF-MS (Selective Reagent Ionization Time-of-Flight Mass Spectrometer) combines the high resolution of PTR-ToF-MS developed at the University of Innsbruck⁴⁰ with the capability of isomeric separation of certain functional groups. This is achieved by taking advantage of the different chemical ionization pathways of specific reagent ions (NO⁺ and H₃O⁺). For example, in the H₃O⁺ mode aldehydes and ketones both exhibit proton transfer and thus both MVK and MACR are detected as C₄H₇O⁺ (m/z 71.050). However, in the NO⁺ mode ketones preferentially cluster with NO⁺ whereas aldehydes are ionized via hydride ion transfer⁹³ and thus MVK is detected as C₄H₆O·NO⁺ (m/z 100.040), whereas MACR is detected as C₄H₅O⁺ (m/z 69.034). The design of the custom built primary ion source of the Innsbruck SRI-ToF-MS allows fast switching between these primary ions and consequently for monitoring of VOC signals virtually in real-time. The E/N in the instruments drift tube was periodically switched between 120 Td, 90 Td and 60 Td in H₃O⁺ mode and 90 Td and 60 Td in NO⁺ mode (E being the electric field strength and N the gas number density; 1 Td = 10⁻¹⁷ V cm²). This helped to identify certain clusters and fragments. The instrument was sampling from inflatable Teflon bags (300 – 400 L) containing the ISOPPOOH standards. Gas standards were prepared by flushing a Teflon T piece containing a septum for ISOPPOOH injection with 3 – 5 slm dry synthetic air (Messer Austria GmbH, 5.0 grade). For the first 30 min after droplet injection the air stream was directed into the hood in order to eliminate residual high volatil-

ity contaminants in part used as solvents for ISOPOOH synthesis and purification. Afterwards the flow was directed into the bag, which had been previously filled with ca. 50 L of synthetic air to reduce possible wall losses of the samples. For introduction of ISOPOOH samples into the SRI-ToF-MS special care was taken to prevent any contact of the sample stream (0.72 slm) with metallic surfaces between the Teflon bag and the drift tube inside the instrument. Therefore, only tubing and fittings made of either Teflon or PEEK were used and the drift tube represented the only metallic surface the sample came in contact with. Both the 1.35 m long inlet line and the drift tube could be heated (maximum temperatures used were 50 °C for the inlet line and 80 °C for the drift tube). For the cold trap experiments, approximately half way between the bag and the SRI-ToF-MS the sampling line insulation was removed and a polystyrene box (20 x 20 x 20 cm), which could be filled with dry ice, was inserted. Before each experiment the Teflon bag was filled with pure synthetic air in order to determine the VOC background. Major ion signals from the sample air could be unequivocally assigned to MVK in the case of 1,2-ISOPOOH and MACR in the case of 4,3-ISOPOOH: in H_3O^+ mode they were detected as $\text{C}_4\text{H}_7\text{O}^+$ (m/z 71.050), and in NO^+ mode 1,2-ISOPOOH was detected as $\text{C}_4\text{H}_6\text{O}\cdot\text{NO}^+$ (m/z 100.040), specific for MVK, whereas 4,3-ISOPOOH was detected as $\text{C}_4\text{H}_5\text{O}^+$ (m/z 69.034), specific for MACR. Negligible signals could be attributed to the parent compound (ISOPOOH) in both NO^+ and H_3O^+ mode independent of the E/N or inlet temperatures used. In the cold trap experiments the MVK respectively MACR signals were largely eliminated, indicating that at least a major part of MVK and MACR is formed after the cold trap. Low volatility ISOPOOHs are expected to be largely frozen out in the cold trap, although this is a function of flow rate. These assumptions are supported by an 1,2-ISOPOOH experiment, in which the dry ice in the cold trap was removed after 75 min, resulting in a large burst of MVK as the cold trap warmed up.

1.6.4 LABORATORY GAS CHROMATOGRAPHY USING CALTECH GC-FID

GC analyses were performed with a commercial gas chromatograph (6890N, Agilent Technologies) equipped with a flame-ionization detector (FID). The carrier gas was hydrogen (UHP H₂, Air Liquide) and the make-up gas was nitrogen obtained from evaporated liquid nitrogen. The analyte gas was sampled through a 0.125" OD perfluoroalkoxy (PFA) Teflon inlet tube. An automatic 6-way stainless steel injection valve directed the analyte gas flow through a 10 mL uncoated stainless steel sample loop, toward either a purge line or the column inlet. The valve box was maintained at 150 °C and the sample loop was continually flushed with the analyte gas mixture. The column inlet, maintained at 155 °C, diluted the injected gas by a ratio of 5:1 with the carrier gas before elution through a bonded polystyrene-divinylbenzene capillary column (HP PLOT-Q, length 15 m, diameter 530 µm) with a nominal flow rate of 10 std. mL min⁻¹. The oven temperature program initiated at 60 °C, and ramped to 250 °C where the oven temperature was held for 3 minutes. The FID detection signals and the column retention times were calibrated with commercial standards of isoprene (Aldrich, > 99% purity), methacrolein (MACR, Aldrich, 95% purity) and methyl vinyl ketone (MVK, Aldrich, 99% purity). The standard compounds were quantified by volume injection, and diluted by calibrated mass flows of nitrogen gas. Gas mixtures of synthesized 1,2-ISOPROOH and 4,3-ISOPROOH standards (200 – 250 ppbv) were created by diluting a measured volume of headspace gas above the standards with nitrogen in inflatable fluorinated ethylene propylene (FEP) Teflon bags with 300 L capacity. The ISOPROOH standard mixture was quantified by CF₃O⁻ chemical ionization mass spectrometry (CIMS)¹⁹, using the sensitivity calibrations previously described.⁸¹ Decomposition of ISOPROOH in the inlet does not occur with the Caltech CIMS as it samples exclusively through PFA Teflon tubing and fluoropolymer coated (Fluoropel, 801A, Cytotix) glass. 1,2-ISOPROOH and 4,3-ISOPROOH were converted to MVK and MACR in the GC, respectively, as evidenced by peaks with identical peak shape and retention times (Fig. 1.2). The

conversion yields were determined by comparing the GC analyses, using the MVK and MACR calibrations under the assumption that the ISOPOOH decomposition occurred before reaching the GC column, with the CIMS analyses. The assumption that decomposition occurred pre-column was supported by the following observations: (1) ISOPOOH sampled by CIMS through a 3 m length of capillary column did not decompose (2) there was no peak broadening or retention time shift, compared to authentic MVK and MACR peaks, that would indicate chemical decomposition in the column, and (3) the most significant factor for conversion was the temperature of the valve box, which is the first metal component to come into contact with the analyte gas stream. Conversion yields of greater than 70% were obtained for the ISOPOOH isomers for the GC methodology described here based on ISOPOOH concentrations determined with the Caltech CF_3O^- CIMS. These experiments were performed during the Focused Isoprene eXperiments at California Institute of Technology (FIXCIT) campaign.⁷⁷

1.6.5 IN-SITU GAS CHROMATOGRAPHY USING NOAA GC-MS

The NOAA instrument is a custom-built, two-channel gas chromatograph coupled to an Agilent (5973N) electron impact (EI) ionization quadrupole mass spectrometer.^{38,37} The NOAA GC-MS is designed for in-situ sampling of a range of volatile organic compounds (VOCs) with immediate analysis. All oxygenated VOCs including methacrolein (MACR) and methyl vinyl ketone (MVK) are detected on the second channel, which is detailed here following a brief description of sample preparation.

Purified liquid standards of 1,2-ISOPOOH and 4,3-ISOPOOH were shipped to NOAA's Earth Systems Research Laboratory in Boulder, CO under dry ice and refrigerated until use. Both standards were initially analyzed via ^1H -NMR (500 MHz) in DMSO-d_6 to ensure sample integrity. For analysis via GC-MS, a few microliters of the pure ISOPOOH standard were drawn into a borosilicate glass capillary tube (1.5 x 50 mm) open at both ends. The capillary tube was then placed inside

a larger PFA sample line (0.25" OD x 10") with PFA bulkhead fittings on both ends. The analyte's gas-phase concentration was diluted by continuously flushing the sample line with 2 slpm of ultra-high purity dry nitrogen (UHP N₂). A polytetrafluoroethylene (PTFE)-diaphragm stainless steel vacuum pump operating at < 2 slpm was used to draw the diluted ISOPOOH sample stream to the GC-MS at super-ambient pressure (1350 kPa). Downstream of the sample pump, 70 sccm of the sample stream is pushed thru a 0.125" OD PFA sample line and two unheated PTFE solenoid valves before entering an ozone trap made of 1 g sodium sulfite (Na₂SO₃) in a 0.25" OD glass tube maintained at 30 °C with PTFE fittings and filters at both ends. From the sulfite trap, the sample stream is plumbed via a 0.125" OD PFA line to a valve oven at 75 °C which contains a 10-port stainless steel switching valve with a polyetheretherketone (PEEK) rotor and then to a water trap (0.125" OD PFA tubing with PFA fittings) at -35 °C. The sample stream exiting the water trap is plumbed via a 0.125" OD PFA line to the aforementioned heated 10-port stainless steel valve, followed by 0.125" OD passivated stainless steel sample line to the sample trap. The sample trap consists of 10 cm of un-coated fused silica tubing (0.53mm ID) at -145 °C via cryogenic cooling. Sample is acquired for 5 minutes at 70 sccm for a total sample size of 350 mL. Post sample acquisition, the sample trap is heated from -145 °C to 35 °C in 5 seconds while UHP He carrier gas flushes the sample from the sample trap to the cryofocus region (Restek Rxi-624Sil, 0.25mm ID, 4 cm) cooled to -165 °C where it is held there for 307 seconds while the channel 1 sample is being analyzed. The cryofocus region then is rapidly heated effectively injecting the sample onto the remainder of the analytical column (Restek Rxi-624Sil, 0.25mm ID, 30m) while flushing with a He carrier gas flow rate of 2 sccm. First, dry UHP N₂ without ISOPOOH was analyzed to ensure the sample stream was free of contaminants. Then 1,2-ISOPOOH in the glass capillary was added to the sample stream. The largest response measured by the NOAA GC-MS was identified as MVK by a) matching the observed retention time (5.30 minutes) to the known retention time of MVK from commercial gas standards and b) comparing the observed EI mass fragmentation pattern to the NIST mass spectral database (Figure 1.8). The

largest peak identified in 4,3-ISOPROOH samples was MACR (retention time = 4.95 minutes, Figure 1.8). Bypassing the sample pump (i.e., completely removing it from the sample path) resulted in substantial decreases in MVK or MACR responses, consistent with the suggestion that the hot stainless steel surfaces, such as that present in the sample pump, may facilitate the conversion of 1,2-ISOPROOH to MVK and 4,3-ISOPROOH to MACR. Tests were repeated with humidified UHP nitrogen as a diluent with no change in results. In order to determine if 1,2-ISOPROOH could be measured on the NOAA GC-MS, we bypassed the sodium sulfite trap and warmed the water trap from -45 °C to +35 °C; however, the parent analyte was never observed. This is in accordance with previous tests that have shown that VOCs containing more than one oxygen atom (e.g., organic acids, diols, or peroxides) cannot be detected by the NOAA GC-MS. We note that both ISOPROOH standards are unusually “sticky” such that the NOAA GC-MS required several days of continuous flushing to reduce the respective MVK or MACR signals to background after these experiments were performed.

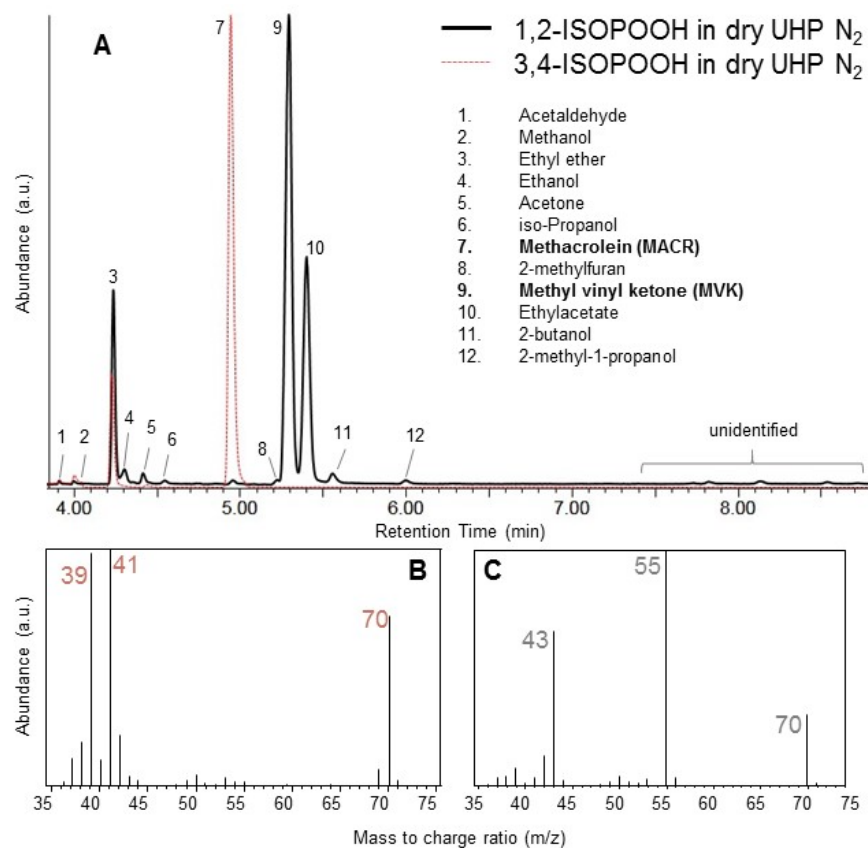


Figure 1.8: A) Total ion chromatograms of 1,2-ISOPPOOH (black trace) and 4,3-ISOPPOOH (red trace) in dry UHP N₂. Two total ion chromatograms are overlaid and scaled so that the heights of the two largest peaks (peak 7: methacrolein and peak 9: methyl vinyl ketone) are equivalent. Electron impact ionization mass spectral fragmentation patterns of B) peak 7 in the 4,3-ISOPPOOH sample is unequivocally identified as methacrolein and C) peak 9 in the 1,2-ISOPPOOH sample is unequivocally identified as methyl vinyl ketone.

1.6.6 ISOPOOH DECOMPOSITION STUDIES

Studies testing the effect of heated metal tubing on ISOPOOH decomposition were conducted using the Caltech CF_3O^- CIMS. ISOPOOH standard was sampled through a 7" long 1/4" O.D. stainless tube inserted into the sampling line at about 1 atm of dry zero air and a residence time of about 1 sec. Transmission changed from 76% at 30 °C to less than 6% at 60 °C, verifying that ISOPOOH readily decomposes on heated metal surfaces, although there appears to be a large passivation effect, as initially transmission was much less and slowly increased over 10's of minutes. In contrast, even at 60 °C virtually no decomposition was observed for PFA Teflon tubing. Similar experiments were also conducted by observing the amount of formaldehyde formed upon sampling through metal tubing as a function of temperature. With increasing temperature of the metal tubing there was a strongly increasing formaldehyde signal, consistent with the proposed interference mechanism. The conversion yield was not calculated as the amount of ISOPOOH introduced into the instrument was not known.

1.6.7 VAPOR PRESSURE CALCULATIONS USING SIMPOL⁸⁰

Group	Value	# for ISOPOOH	# for MVK	# for MACR
constant term	1.79	1	1	1
carbon number	-0.438	5	4	4
alkene	-0.105	1	1	1
enone	-0.506	0	1	1
hydroxyl	-2.23	1	0	0
aldehyde	-1.35	0	0	1
ketone	-0.935	0	1	0
hydroperoxy	-2.48	1	0	0
Pvap exponent		-5.215	-1.508	-1.923
Pvap (atm)		6.1×10^{-6}	3.1×10^{-2}	1.2×10^{-2}

I.6.8 OH REACTIVITY CALCULATED FROM MCM V3.2

Compound	k_{X+OH} at 298 K ^{a)}	relative yield ^{b)}	OH reactivity ^{d)}
MVK	2.014×10^{-11}	0.415	$0.5 \text{ s}^{-1} \text{ ppb}^{-1}$
MACR	2.863×10^{-11}	0.265	$0.7 \text{ s}^{-1} \text{ ppb}^{-1}$
(MVK+MACR)	2.345×10^{-11}		$0.6 \text{ s}^{-1} \text{ ppb}^{-1}$
1,2-ISOPROOH	5.0×10^{-11}	0.444	$1.3 \text{ s}^{-1} \text{ ppb}^{-1}$
4,3-ISOPROOH	1.15×10^{-10}	0.306	$2.9 \text{ s}^{-1} \text{ ppb}^{-1}$
ISOPROOH ^{c)}	8.85×10^{-11}		$2.2 \text{ s}^{-1} \text{ ppb}^{-1}$
$\delta(\text{reactivity})$			$1.6 \text{ s}^{-1} \text{ ppb}^{-1}$
$\delta(\text{scaled reactivity})^e)$			$2.9 \text{ s}^{-1} \text{ ppb}^{-1}$

a) in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

b) yield of 1,2-ISOPROOH and 4,3-ISOPROOH via reaction of isoprene with OH and accounting for nitrate formation for reaction with NO.

c) for this case the weighted average of 1,2-ISOPROOH and 4,3-ISOPROOH, as these isomers are detected as MVK/MACR assuming an air number density of $2.5 \times 10^{19} \text{ molec cm}^{-3}$ scaled by a detection efficiency of 57%, the average determined for PTR and GC in this work.

I.6.9 EFFECT ON ESTIMATED OH FROM MVK+MACR/ISOPRENE RATIOS

The reaction rate of ISOPROOH with OH is 3-4 that for MVK/MACR and the yield of ISOPROOH from $\text{RO}_2 + \text{HO}_2$ is >85%. The analytical expression for a sequential reaction (eq. 5a, 5b in ref. ⁵⁶) was used by Karl et al. to estimate OH concentrations from the ratio of oxidation product to isoprene.

$$\frac{[MVK + MACR]}{[Isoprene]} = 0.55 \frac{k_{I+OH}}{k_{M+OH} - k_{I+OH}} (1 - e^{((k_{I+OH} - k_{M+OH})[OH]t)})$$

$$t := \frac{z_i}{w^*}$$

k_I is the reaction rate constant of isoprene + OH, k_M is the average reaction rate constant of (MVK and MAC) + OH, z_i is the altitude, w^* is the convective velocity scale, estimated at 1.9 m/s, and t is the reaction time. The method assumes that the vertical transport is analogous to a flow tube reaction with a vertical velocity of 1.9 m/s. Figure 1.9 shows the calculated ratios of [MVK+MACR]/isoprene for $[\text{OH}] = 6 \times 10^6 \text{ molec cm}^{-3}$ and $[\text{OH}] = 3 \times 10^6 \text{ molec cm}^{-3}$. Also shown are the corresponding [ISOPOOH]/isoprene ratios calculated by substituting the average rate constant of MVK+MACR with OH with that of the mean value of 1,2- and 4,3-ISOPOOH of $8 \times 10^{-11} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (MCM). Also the yield of 55% for MVK+MACR used by Karl et al. is substituted by the yield of ISOPOOH, which is greater than 85%. Different ratios result for the same OH concentration ($6 \times 10^6 \text{ molec cm}^{-3}$) depending on which product is assumed. Clearly, conclusions drawn on the basis of MVK and MACR need to be reevaluated as the chemical properties of ISOPOOH differ from those of MVK and MACR.

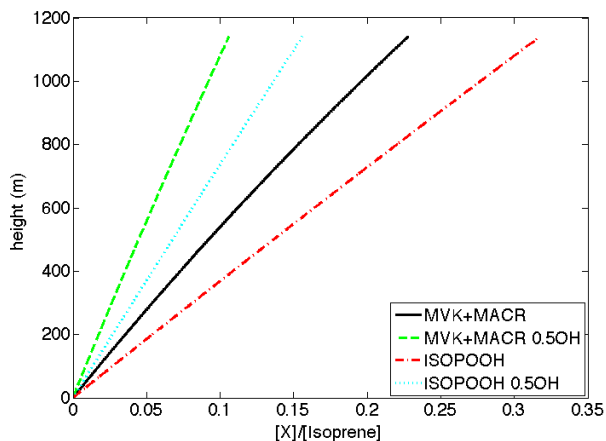


Figure 1.9: Calculated product/isoprene ratios as a function of altitude

1.6.10 OH RECYCLING FROM MVK+MACR/ISOPRENE RATIOS AT $\text{NO} = 0$, O:C RATIO AND OH REACTIVITY

The reaction of ISOPOOH with OH fully recycles OH via formation of IEPOX. In contrast the oxidation of MVK and MACR by OH forms HO_2 and not OH according to the MCM v3.2.^{51,52,90}

The figure shows the difference in OH recycling under pristine conditions as a function of the contribution of ISOPOOH to the measurement. The blue dotted line includes the OH recycling mechanism from MACR described by Crounse^{18,58} et al., which is largely independent of NO. The effects on oxidative capacity via both the OH sink strength (reactivity) and the OH recycling fraction vary strongly with the fraction of pristine product. Depending on the conditions the two might balance each other. The O:C ratio is much larger if the observed products are ISOPOOH than if they are MVK+MACR.

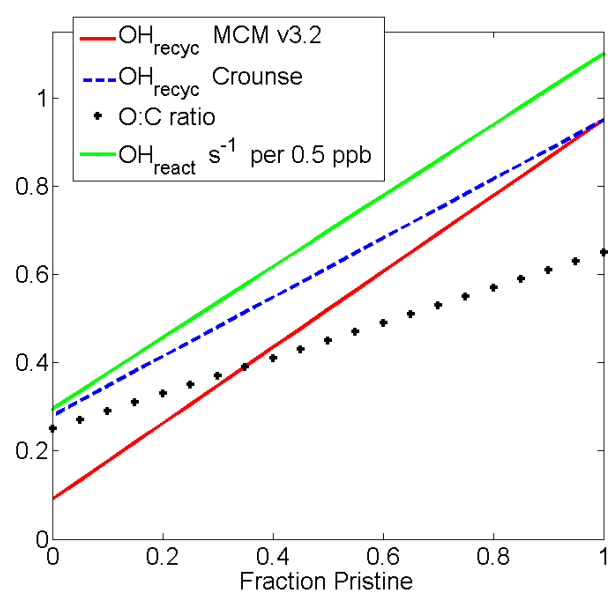


Figure 1.10: O:C ratio, OH recycling, and OH reactivity as a function of pristine contribution to observed products.

2

Measurements of Henry's Law constants and aqueous-phase oxidation of isoprene hydroxy hydroperoxides

2.1 ABSTRACT

ISOPRENE HYDROXYHYDROPEROXIDES (ISOPOOHs) are the main first-generation products of isoprene oxidation under low- NO_x conditions. ISOPOOHs contain two highly hydrophilic functional groups that enable them to partition into atmospheric waters. Henry's Law constants

for two ISOPOOH isomers were measured. Their Henry's Law constants differed by an order of magnitude which was not captured by models. We also conducted aqueous photooxidation experiments aimed at understanding the behavior of ISOPOOH after partitioning to the aqueous-phase. ISOPOOH standards were irradiated in the presence of H_2O_2 to simulate in-cloud oxidation. The solutions were analyzed online via High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometry (HR-ToF-CIMS) and High-Resolution Time-of-Flight Aerosol Mass Spectrometry (HR-ToF-AMS). We were able to determine that the main products of ISOPOOH oxidation in water are isoprene epoxydiols (IEPOX). Side products formed during the photooxidation were detected as well, including highly oxygenated compounds and products of direct photolysis like OH. We observed an increase in organic to sulfate ratio and oxidation state in the particle phase as the experiment proceeds. ISOPOOH was confirmed to produce OH in the condensed phase via direct photolysis. Finally, competition experiments with Levoglucosan allowed for the measurement of ISOPOOHs OH reaction rate constant in the condensed phase. The importance of organic hydroperoxides will continue to increase as environmental regulations shift atmospheric conditions towards preindustrial levels. Together these experiments provide new insights into the role that hydroperoxides can play in SOA formation via cloud processing.

2.2 INTRODUCTION

Hundreds of teragrams of reactive carbon are emitted into the atmosphere every year.^{41,82} The majority of the carbon is oxidized in the gas phase via photochemical processes. Oxidation is typically initiated by the hydroxyl radical (OH) and the resulting distribution of products is modulated by the levels of nitrogen oxides (NO_x) in the atmosphere.³ While oxidation proceeds the properties of these compounds change as oxygenated functional groups are introduced. Under preindustrial conditions or in remote locations (low- NO_x), the introduction of alcohol, hydroperoxide and car-

boxylic acid groups can significantly increase the compounds' water solubility, allowing them to partition into atmospheric waters like clouds and fog. This contrasts with high- NO_X oxidation under modern conditions whose products are often carbonyls with relatively low solubility.

Recently, attention has shifted from gas-phase oxidation towards oxidation processes in the condensed phase. The oxidation of water soluble compounds in clouds and fogs is known as aqueous processing. This process is responsible for a large portion (64-83%) of the oxidation of sulfur dioxide (SO_2) into sulfuric acid (H_2SO_4).⁴⁴ Similarly, the oxidation of compounds that partition into cloud water via aqueous processing has been suggested as a potentially large source of secondary organic aerosols (SOA). Specifically, in cloud oxidation has been suggested to lead to low volatility compounds like oxalic acid that remain in the particle phase after clouds evaporate.³² SOA formed via this pathway is known as aqueous SOA (aqSOA) and is the subject of intensive research.^{46,31}

Glyoxal, a high- NO_X product of isoprene oxidation, has been well studied in this context. It's oxidation has been shown to produce oxalic acid, a known constituent of cloud water.¹⁰ The total abundance of glyoxal (40 Tg C yr^{-1}), its reaction rate with OH, solubility in water and SOA yield make it an important compound in cloud processing. Similarly, isoprene hydroxyl hydroperoxides (ISOPOOH) are potential candidates for efficient aqueous processing. They are the main first-generation oxidation products of isoprene (180 Tg C yr^{-1}) under low- NO_X conditions. In one oxidation step the isoprene carbon skeleton gains a hydroperoxyl and a hydroxyl group, increasing the compounds solubility in water by multiple orders of magnitude. This contrasts with products of high- NO_X oxidation, whose fragmentation and functionalization often lead to minimal enhancements in Henry's Law constants.⁸⁹ ISOPOOHs also retain a carbon-carbon double bond, which contributes to their fast gas-phase OH reaction rate.⁹⁵ There are 6 isomers of ISOPOOH, the most abundant being the β -hydroxyhydroperoxides (1,2-ISOPOOH and 4,3-ISOPOOH), which are the subject of this work.

In the gas phase, their reaction with OH has been shown to make isoprene epoxydiols (IEPOX)⁸¹

and other low-volatility compounds.⁶¹ ISOPOOH is also a representative of a relatively understudied group of atmospheric compounds: organic hydroperoxides. Like ISOPOOH, these compounds are readily formed in the atmosphere under low-NO_x conditions from the reaction of RO₂ radicals with HO₂ and via autooxidation reactions. However, due to their innate instability these compounds are difficult to measure without specialized instruments like chemical ionization mass spectrometers (CIMS) with CF₃O⁻, I⁻ and other reagent ions^{19,64} or a more labor intensive method like High-Pressure Liquid Chromatography (HPLC) after derivatization.⁴⁸ The use of gas chromatography (GC) or proton transfer reaction mass spectrometry (PTR-MS) often leads to misidentification and possibly interferences.⁸⁶ Hydroperoxides are also highly water soluble and their oxidation is often OH neutral. Photolysis of labile hydroperoxides could also be a source of OH radicals in the condensed phase.⁶⁸

Previous aqueous processing work has focused on high-NO_x isoprene oxidation products, including glyoxal (CHOCHO) and methylglyoxal (MGly),⁶⁷ methacrolein (MACR) and methylvinylketone (MVK),¹⁰⁸ in part due to their commercial availability and chemical stability. The oxidation of C₄ diols (products of IEPOX oxidation) has also been reported.⁷⁹ The oxidation of only the simplest organic hydroperoxides has been studied in the condensed phase.⁷⁶ This work explores the bulk-phase aqueous phase oxidation of ISOPOOH and by extension IEPOX. Using synthesized standards of two ISOPOOH isomers (1,2-ISOPOOH and 4,3-ISOPOOH), we performed measurements of ISOPOOHs Henrys Law constant (K_H), its aqueous phase reaction rate with OH (k_{OH}), and investigated the products of its OH initiated oxidation. Experiments were performed using a combination of CF₃O⁻ CIMS, I⁻ CIMS and HR-ToF-AMS. This instrument suite provides online measurements of both the aqueous phase and the aerosol generated from these solutions. This data set improves our understanding of the role of organic hydroperoxides in SOA formation through cloud processing.

2.3 EXPERIMENTAL SECTION

All reagents were purchased from Sigma-Aldrich and used without further purification. The synthesis of ISOPOOH (described below) is an explosion hazard. Never concentrate reaction mixtures without removing the catalyst via filtration through silica gel. After purification, ISOPOOH can be concentrated and was stored in a -20 °C freezer for months without appreciable decomposition. Solutions in water are also stable but should not be allowed to freeze. Reactions were monitored via thin layer chromatography (TLC) using a potassium permanganate stain for visualization.

2.3.1 SYNTHESIS OF ISOPOOH

SYNTHESIS OF 1,2-ISOPOOH

This procedure was adapted from the method published by Li⁶⁶ and is summarized here for your convenience:

PREPARATION OF ETHEREAL HYDROGEN PEROXIDE ($\text{H}_2\text{O}_2 \cdot \text{Et}_2\text{O}$) — A solution of hydrogen peroxide (30% in H_2O) (30 mL) was saturated with sodium chloride. Excess salt was filtered out. Hydrogen peroxide was transferred to diethyl ether by washing a 10-mL portion of diethyl ether with four 6 mL portions of the NaCl saturated hydrogen peroxide solution. The resulting organic fraction was dried with MgSO_4 , filtered and used as solvent for the epoxide ring opening reaction.

EPOXIDE RING OPENING — 2-methylvinylloxirane (1 mmol) was dissolved in $\text{H}_2\text{O}_2 \cdot \text{Et}_2\text{O}$ (5 mL) and stirred. 5 mg of phosphomolybdic acid was added to the solution. Upon addition, the reaction turned dark blue and faded to yellow as the reaction progressed. The reaction was stirred for 6 h after which the solution was diluted with Et_2O and then filtered through a small amount of silica to remove the phosphomolybdic acid. The silica was washed with Et_2O to recover all the product.

The organic layer was then evaporated and purified using a flash chromatography using 90:10 Hexane:EtOAc as the mobile phase. Using an 85:15 ratio makes the column faster at the expense of separating H₂O₂ from 1,2-ISOPOOH. ¹H NMR (400 MHz, DMSO-d₆) δ 10.88 (s, 1H), 5.93 (dd, J = 17.9, 11.1 Hz, 1H), 5.18 (dd, J = 17.8, 1.4 Hz, 1H), 5.12 (dd, J = 11.1, 1.4 Hz, 1H), 4.53 (t, J = 6.2 Hz, 1H), 3.43 (dd, J = 11.4, 5.9 Hz, 1H), 3.35 (dd, J = 11.5, 6.5 Hz, 1H), 1.17 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 140.36, 114.95, 83.71, 64.72, 19.01.

SYNTHESIS OF 4,3-ISOPOOH

The synthesis of 4,3-ISOPOOH has been previously described.⁷³ Briefly, 3.3 mL of acetonitrile were saturated with O₂ by bubbling the solvent with an oxygen filled balloon for 20 minutes. Prenol (100 uL, 1 mmol) and methylene blue (5.3 mg, 0.01 mmol) were added to the solution. The oxygen balloon was removed from the solution but still attached to the flask. The reaction was irradiated with a 16 W LED light bulb for 6 hours and monitored by TLC. After consumption of the starting material, the solution was filtered through a small plug of silica. The silica was washed with Et₂O to recover any product. The solvent was then evaporated and the residue purified via flash-column chromatography using 85:15 Hexane:EtOAc as the mobile phase. ¹H NMR (400 MHz, DMSO-d₆) δ 11.42 (s, 1H), 4.94 – 4.83 (m, 2H), 4.72 (t, J = 5.9 Hz, 1H), 4.21 (dd, J = 6.5, 4.9 Hz, 1H), 3.52 – 3.34 (m, 2H), 1.67 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 142.91, 113.19, 89.30, 61.12, 30.68.

HENRY'S LAW CONSTANT DETERMINATION

Experiments were carried out by dissolving a known amount of 1,2-ISOPOOH, 4,3-ISOPOOH, or H₂O₂ in water (10 mL). The solution was transferred to a 3-neck round bottom flask and stirred gently with a magnetic stir bar. The flask was previously coated with FluoroPel (PFC 802A) to reduce wall losses and equilibration time. Zero air was flowed across the flask, entering and sam-

pled from opposite sides. Air coming out of the flask was diluted with nitrogen before analysis by CF_3O^- CIMS, as previously described.¹⁹ The air flow through the flask was calculated from the difference between the flow into the instrument (133.6 sccm) and the dilution flow, which was controlled by a 200 sccm mass flow controller (MFC). The MFC was set to 119 sccm and 126.4 sccm during the lower flow experiment. Flows going through the flask were 14.6 sccm and 7.2 sccm respectively. The total volume in the flask was 134 cm^3 . Excluding the 10 cm^3 sample volume, the residence times in the flask were 8.5 and 17 minutes respectively. 1,2-ISOPOOH experiments were carried out at 103 mM concentrations. The 4,3-ISOPOOH isomer was significantly less soluble; experiments were carried out at 24.9 mM and 5 mM. Observed K_H did not change when accounting for the different concentrations and flow-rates. This indicates good equilibration within the flask and sampling lines.

Experiments were carried out with each ISOPOOH isomer (3 replicates) to determine the temperature dependence of their K_H . The solutions were cooled with a water ice bath to $0\text{ }^\circ\text{C}$ and then allowed to warm to room temperature ($23\text{ }^\circ\text{C}$). Unfortunately, measurements near room temperature often suffered from water condensation on the lines due to room temperature changes. For this reason, we used the data from 0 to $20\text{ }^\circ\text{C}$ and extrapolated the K_H values at $25\text{ }^\circ\text{C}$.

AQUEOUS PHOTOOXIDATION EXPERIMENTS

The experimental set-up for the aqueous photooxidation experiments was described in detail by Zhao et al.¹⁰⁹ and was slightly modified for this set of experiments (Figure 2.1). Stock solutions of each ISOPOOH isomer were made by dissolving a weighed sample of ISOPOOH of known purity in water. These solutions were then diluted to a known concentration (100, 66 or $33\text{ }\mu\text{M}$) to perform three types of photooxidation experiments. Product experiments were performed using a mercury 254 nm lamp with and without adding H_2O_2 . These experiments were designed to determine the products and kinetics of ISOPOOH oxidation with OH as well as the properties of particles

generated from these solutions. The solutions were also 100 μM in ammonium sulfate to generate particles after atomization. A second type of experiment employed UV-B illumination and a high concentration (1 mM) of benzoic acid to trap any OH formed in solution. These experiments were used to determine photolysis rates of ISOPOOH isomers as well as the OH yield from these processes. Finally, experiments were carried out in the presence of levoglucosan to determine the OH reaction rate of ISOPOOH isomers via competition experiments. Control experiments were performed by irradiating ammonium sulfate solutions or solutions with only H_2O_2 . OH levels during the experiments were in the 10^{-13} M range,¹⁰⁹ relevant for cloud oxidation.

Sampling was performed by atomizing part of the aqueous solution and directing the resulting aerosol through a heated line where volatiles were analyzed online via HR-ToF-CIMS using iodide as a reagent ion. Some of the experiments were also sampling the atomized solutions using an HR-ToF-AMS to investigate the properties of the aerosol as oxidation proceeds. A diffusion drier was present before the AMS and was by-passed in one of the experiments to probe the effect of water content on aerosol properties. The analysis of ISOPOOH data is complicated by the fact that the main product, β -IEPOX, is an isomer. During our experiments, it was found that the I^- CIMS sensitivity to some compounds is highly dependent on the pH of the solution. The signal from IEPOX is greatly diminished, but not eliminated, at pH 4, while that of ISOPOOH remains the same. Performing experiments under these conditions, the decay of ISOPOOH can be observed. However, to observe the most products, experiments aimed at elucidating the mechanism of aqueous oxidation were performed at close to neutral pH values and then analyzed using the information gathered from the low pH experiments. For the same reasons, competition experiments were carried out at pH 4. For the OH production experiments, benzoic acid was chosen as the OH “trap” since it has a fast reaction rate with OH, it lowers the pH to 4 and its main products, hydroxybenzoic acids, are observable by I^- CIMS.

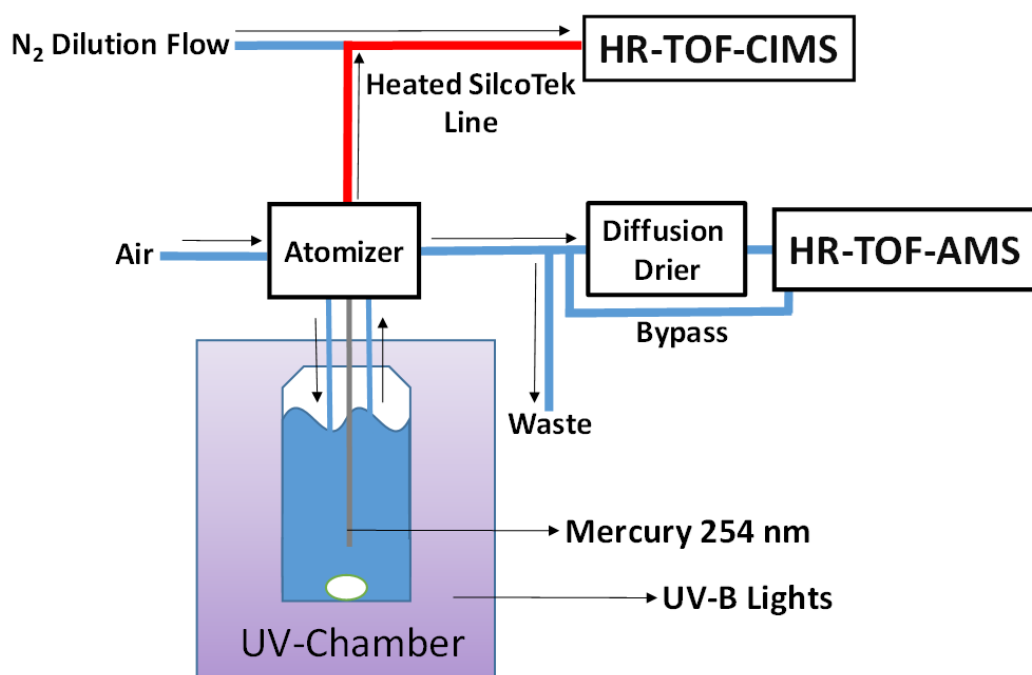


Figure 2.1: Aqueous-phase photooxidation experimental set-up.

2.4 RESULTS

2.4.1 HENRY'S LAW CONSTANT (K_H) MEASUREMENTS

K_H was measured using a flow through method. Briefly, an aqueous ISOPOOH solution (10 mL) of known concentration was placed in a multi-neck round bottom flask and cooled in an ice bath while stirring gently. A small flow of air (<15 sccm) was introduced from one side of the flask and sampled through the opposite side using a CF_3O^- CIMS. As the ice melted, the solution warmed up to room temperature while sampling continuously. Temperature changed less than 0.2 K per minute; the increase in temperature slowed down as the solution approached room temperature. The temperature dependence of K_H was determined by performing three repeat experiments with each ISOPOOH isomer. The experiments carried out with 4,3-ISOPOOH were performed with 2 different concentrations and flow rates to test for proper equilibration within the flask. K_H and its temperature dependence did not change when varying concentration or flow rate. An experiment with H_2O_2 was used to validate our flow-through method. Data from the experiments was plotted according to the van't Hoff equation (Figure 2.2):

$$\ln(K_H) = \frac{(A)}{T} + B$$

Using this method, K_H for H_2O_2 at 298 K was determined to be $1.19 \times 10^5 \text{ M} \cdot \text{atm}^{-1}$. This is higher than previously reported values⁹⁹ which range from 6.7×10^4 to $1.05 \times 10^5 \text{ M} \cdot \text{atm}^{-1}$. Our values are within previous experimental determinations at low temperatures (see Figure 2.3 for a comparison). A list of experiments and the determined Henry's law constants and parameters are shown in Table 2.1. 1,2-ISOPOOH has the highest K_H with a value of $1.18 \times 10^5 \text{ M} \cdot \text{atm}^{-1}$ at 298 K. At the same temperature, the 4,3-ISOPOOH isomer has a K_H of $1.21 \times 10^4 \text{ M} \cdot \text{atm}^{-1}$. Despite being regioisomers, the Henry's law constants for these hydroxyl hydroperoxides differ by an order of magnitude.

The lower solubility and Henry's Law constant for 4,3-ISOPROOH suggest it behaves as a significantly more hydrophobic molecule.

The Henry's Law constants determined in this work were compared with modeled values. Henry's Law constants were calculated using two different models: GROMHE⁸⁴ and EVAPORATION¹⁷+AIOMFAC¹¹⁰. The latter is a combination of two models and their output is used to calculate K_H as follows:

$$K_H = cw \cdot (p_0 \cdot g)^{-1}$$

Where cw is 55.6 M, p_0 is the compounds' vapor pressure (predicted by EVAPORATION) and g is the activity coefficient (predicted by AIOMFAC).

GROMHE predicts a K_H of $1.3 \times 10^6 \text{ M} \cdot \text{atm}^{-1}$ and no difference between isomers. EVAPORATION+AIOMFAC predicts a K_H of $1.0 \times 10^5 \text{ M} \cdot \text{atm}^{-1}$ for 1,2-ISOPROOH which is very close to the experimental value determined during this work. However, it predicts a Henry's law constant of $2.6 \times 10^5 \text{ M} \cdot \text{atm}^{-1}$ for 4,3-ISOPROOH. This is higher than the value for 1,2-ISOPROOH contradicting observed K_H values. Table 2.2 summarizes the values determined in these experiments and simulations. Determinations of K_H for other multifunctional hydroperoxides are needed to develop reasonable structure-activity relationships and improve the performance of these models.

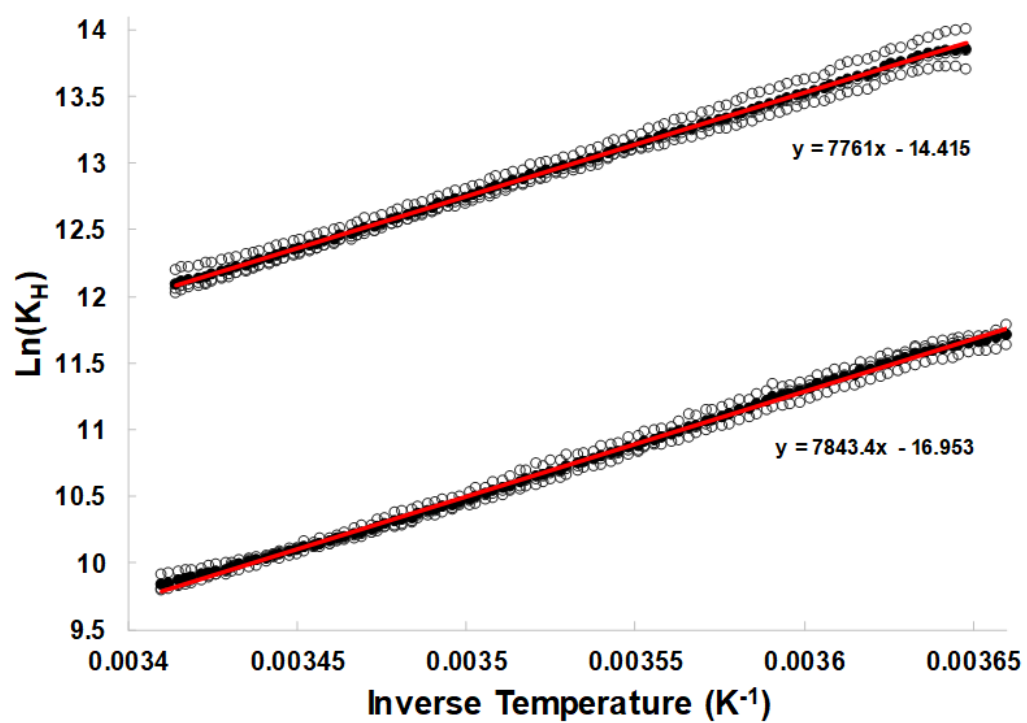


Figure 2.2: Van't Hoff plot of Henry's Law constant experiments for 1,2-ISOPROOH (top) and 4,3-ISOPROOH (bottom). o = individual experiments (3 replicates for each isomer) ● = average - = best linear fit

Henry's Law Experiment Table						
#	ISOPOOH	[Concentration]	Flow Rate	A	B	K_H (25 °C) M·atm ⁻¹
1	1,2	103 mM	14.6 sccm	7568	13.7	1.19x10 ⁵
2	1,2	103 mM	14.6 sccm	8007	15.24	1.11x10 ⁵
3	1,2	103 mM	14.6 sccm	7936	14.88	1.25x10 ⁵
4	4,3	24.6 mM	14.6 sccm	8142	17.93	1.18x10 ⁴
5	4,3	4.98 mM	14.6 sccm	7818	16.83	1.20x10 ⁴
6	4,3	4.98 mM	7.2 sccm	8316	18.47	1.24x10 ⁴
7	H ₂ O ₂	98 mM	14.6 sccm	5934	8.217	1.19x10 ⁵

Table 2.1: Experimental conditions and values obtained during our Henry's Law determinations

Summary of Henry's Law constants (M·atm ⁻¹) determined in this work				
Species	KH 5 °C	KH 25 °C	E + A 25 °C	GROMHE 25 °C
1,2-ISOPOOH	1.3×10 ⁶	1.18×10 ⁵	1×10 ⁵	1.3×10 ⁶
4,3-ISOPOOH	7.3×10 ⁴	1.20×10 ⁴	2.6×10 ⁶	1.3×10 ⁶
H ₂ O ₂	4.97×10 ⁵	1.19×10 ⁵	N/A	N/A

Table 2.2: Comparison between modeled and experimentally determined K_H values (E+A = Evaporation + AIOMFAC)

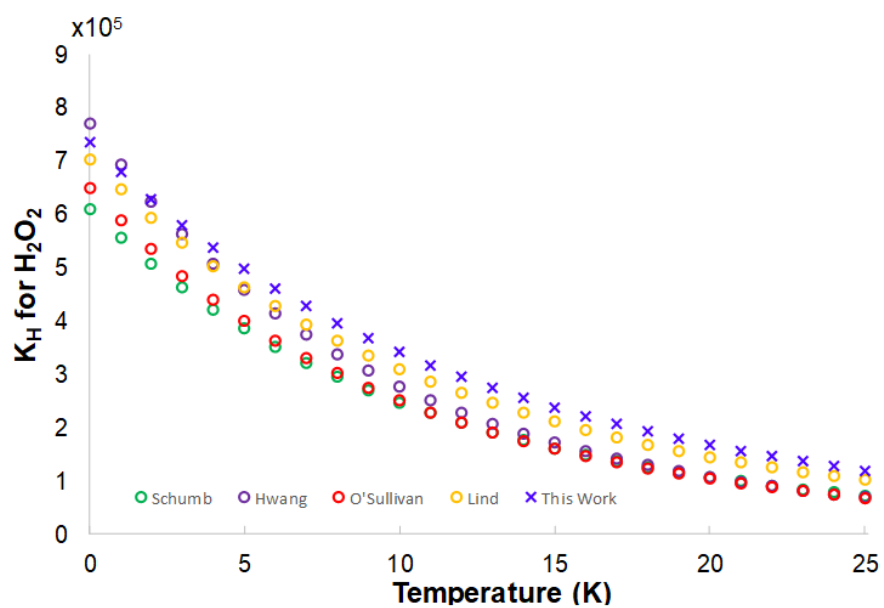


Figure 2.3: Comparison of Henry's Law constants ($\text{M}\cdot\text{atm}^{-1}$) for H_2O_2 . Methodology for the other experiments are described in their respective articles and are plotted according to the data compiled by O'Sullivan.⁹⁹ Our H_2O_2 experiment is close to the data published previously.

2.5 ISOPOOH REACTION RATE WITH OH

The ISOPOOH reaction rate with OH was investigated via the relative rates method. Levoglucosan was used for competition since it can be measured using the same experimental set-up and its OH reaction rate was measured previously.¹⁰⁹ The data is shown in figure 2.4 for both 1,2-ISOPOOH and 4,3-ISOPOOH. Based on this data, k_{OH} for 1,2-ISOPOOH is $(2.6 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ while k_{OH} for 4,3-ISOPOOH is $(2.4 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. To account for photolysis, experiments were performed in the presence of benzoic acid as an OH scavenger and under similar illumination conditions (254 nm light, figure 2.5) affording photolysis rates of $3.4 \times 10^{-4} \text{ s}^{-1}$ and $3.0 \times 10^{-4} \text{ s}^{-1}$ for 1,2-ISOPOOH and 4,3-ISOPOOH respectively. These photolysis rates were subtracted from the observed ISOPOOH decays before calculating k_{OH} . The values for the reaction rate of ISOPOOHs with OH are in line with those expected from alkenes with electron withdrawing groups on vicinal carbons.⁸

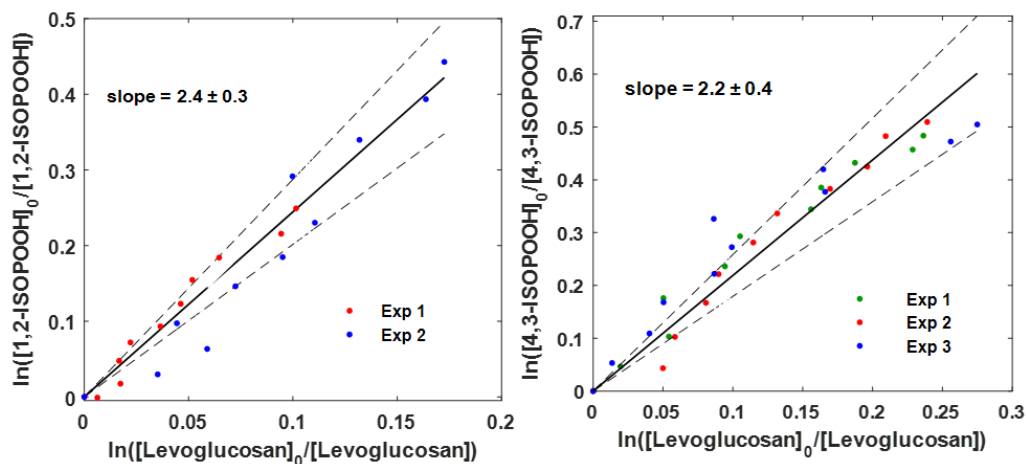


Figure 2.4: Competition experiments of 1,2-ISOPROOH (left) and 4,3-ISOPROOH (right) against levoglucosan affords a $(2.6 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $(2.4 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ reaction rate against OH, respectively.

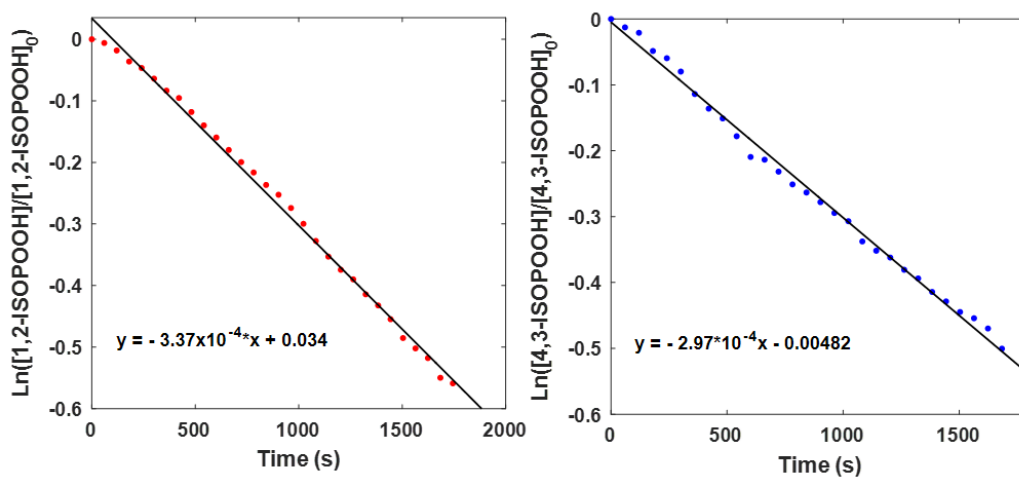


Figure 2.5: Photolysis experiments of 1,2-ISOPROOH (left) and 4,3-ISOPROOH (right). These rates were used to correct the levoglucosan competition experiments. Losses due to photolysis were subtracted from the observed reaction rate and reported as k_{OH} .

2.6 AQUEOUS PHASE OXIDATION PRODUCTS

Figure 2.6 shows an oxidation experiment of 1,2-ISOPROOH and the behavior of compounds previously shown to contribute to SOA. Time traces for all products are shown in figures 2.7-2.11. The main product of ISOPROOH oxidation is IEPOX. The unusual shape of the $C_5H_{10}O_3$ time trace is due to the fact ISOPROOH and IEPOX are isomers with different sensitivities. Oxygen addition and photolysis competes with IEPOX formation. Oxygen addition to aqueous organic radicals proceeds at $10^9 \text{ M}^{-1}\text{s}^{-1}$, a value that is 1000 times faster than the rates used in previous aqueous oxidation models.^{100,91} With a saturated oxygen concentration of $2.6 \times 10^{-4} \text{ M}$ the ISOPROOH+OH radical has a lifetime against O_2 of 4 μs . After O_2 addition the peroxy radical ($C_5H_{11}O_6$) can undergo RO_2 - RO_2 and RO_2 - HO_2 chemistry along with unimolecular isomerization reactions. The products expected from RO_2 - RO_2 chemistry include direct formation of $C_5H_{12}O_5$ and $C_5H_{10}O_5$ (via the Russell mechanism) as well as fragmentation products like $C_4H_8O_4$, CH_2O (observed as the hydrate CH_4O_2), $C_3H_6O_2$ and $C_2H_4O_2$.¹⁰² Indeed, formation of $C_5H_{12}O_5$ in 1,2-ISOPROOH is primary as observed in figure 2.11, but this product cannot be formed as a primary product from the equivalent $C_5H_{11}O_6$ RO_2 generated from 4,3-ISOPROOH. $C_5H_{12}O_5$ is observed as a secondary product in 4,3-ISOPROOH implying that scrambling of the RO_2 isomer, if any, might be limited.⁵⁴ $C_5H_{10}O_5$ can be formed from other compounds, including IEPOX and possibly via isomerization reactions.²⁴

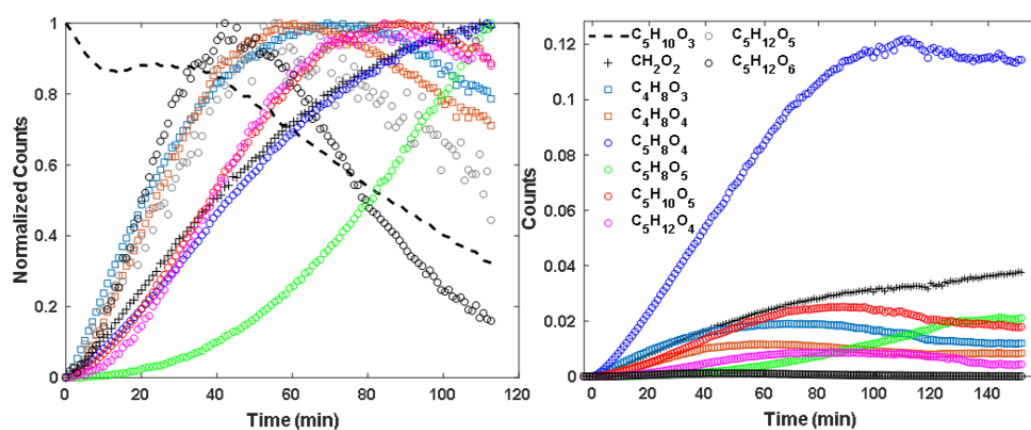


Figure 2.6: 1,2-ISOPROOH oxidation products that have been previously observed in the particle phase. Normalized traces (left) show a large contribution from first-generation ISOPROOH oxidation products. The product counts (right) are dominated by CH_2O_2 , $\text{C}_5\text{H}_8\text{O}_4$ and $\text{C}_5\text{H}_{10}\text{O}_5$.

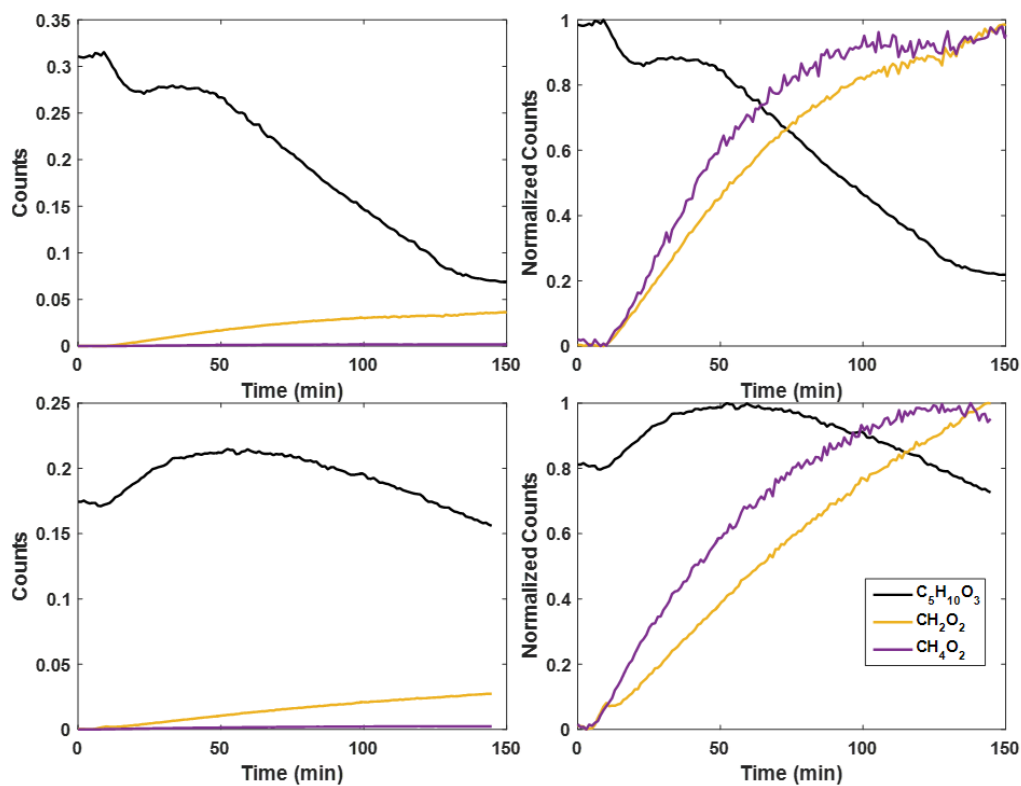


Figure 2.7: Traces of the one carbon products from the oxidation of 1,2-ISOPROOH (top) and 4,3-ISOPROOH (bottom). On the left are the observed counts and on the right there are the counts normalized to one. CH_2O_2 is likely formic acid and CH_4O_2 is likely hydrated formaldehyde.

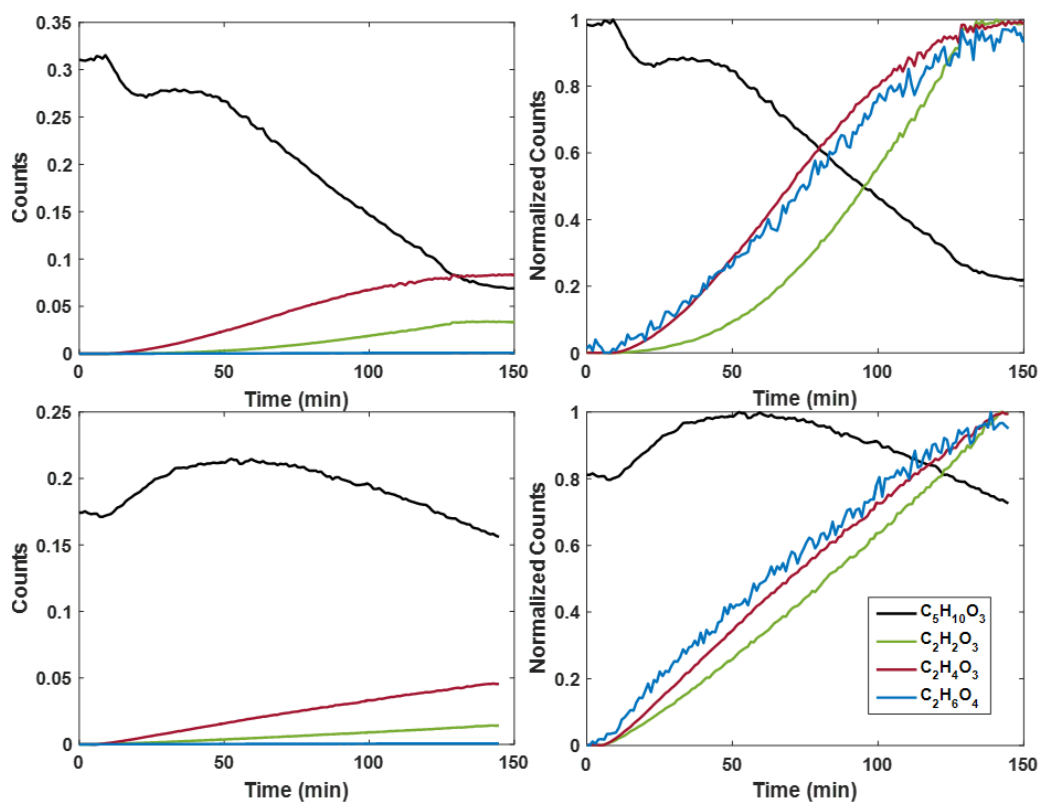


Figure 2.8: Traces of the two carbon products from the oxidation of 1,2-ISOPROPOH (top) and 4,3-ISOPROPOH (bottom). On the left are the observed counts and on the right there are the counts normalized to one. $C_2H_2O_3$ is likely glyoxylic acid, $C_2H_4O_3$ and $C_2H_6O_4$ could be glyoxal mono and dihydrate respectively.

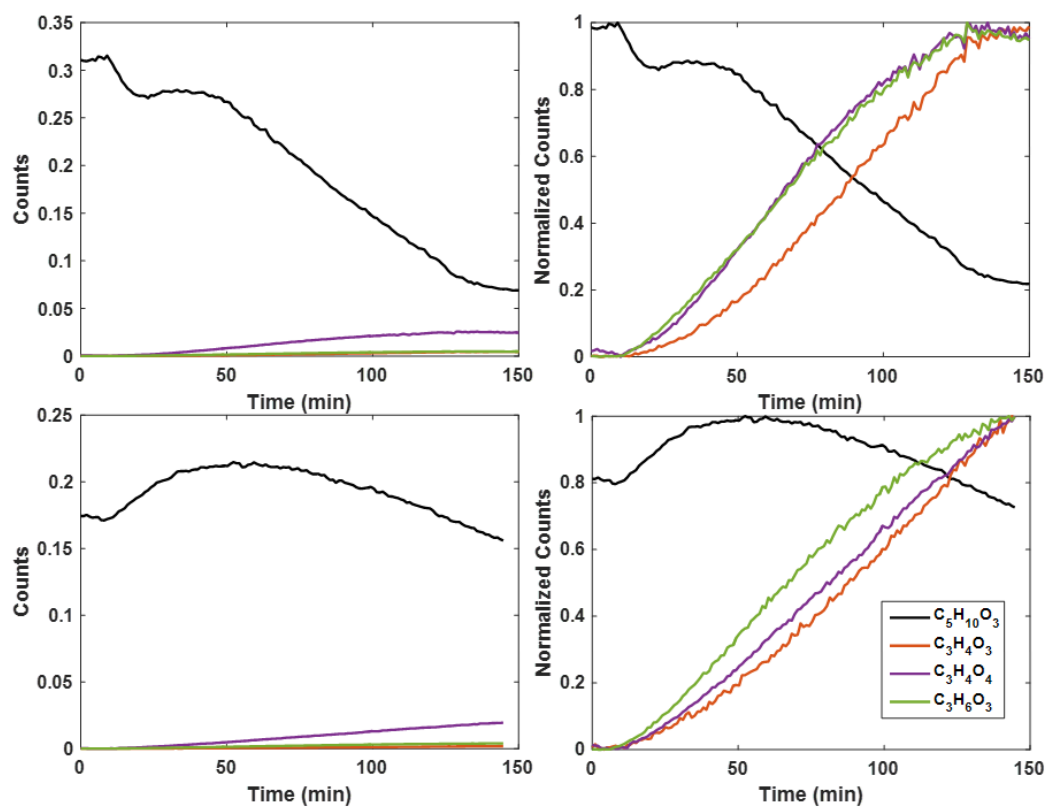


Figure 2.9: Traces of the three carbon products from the oxidation of 1,2-ISOPOOH (top) and 4,3-ISOPOOH (bottom). On the left are the observed counts and on the right, there are the counts normalized to one. $C_3H_6O_3$ is likely hydrated methylglyoxal, $C_3H_4O_4$ and $C_3H_4O_3$ seem like oxidation products of methylglyoxal including pyruvic acid.

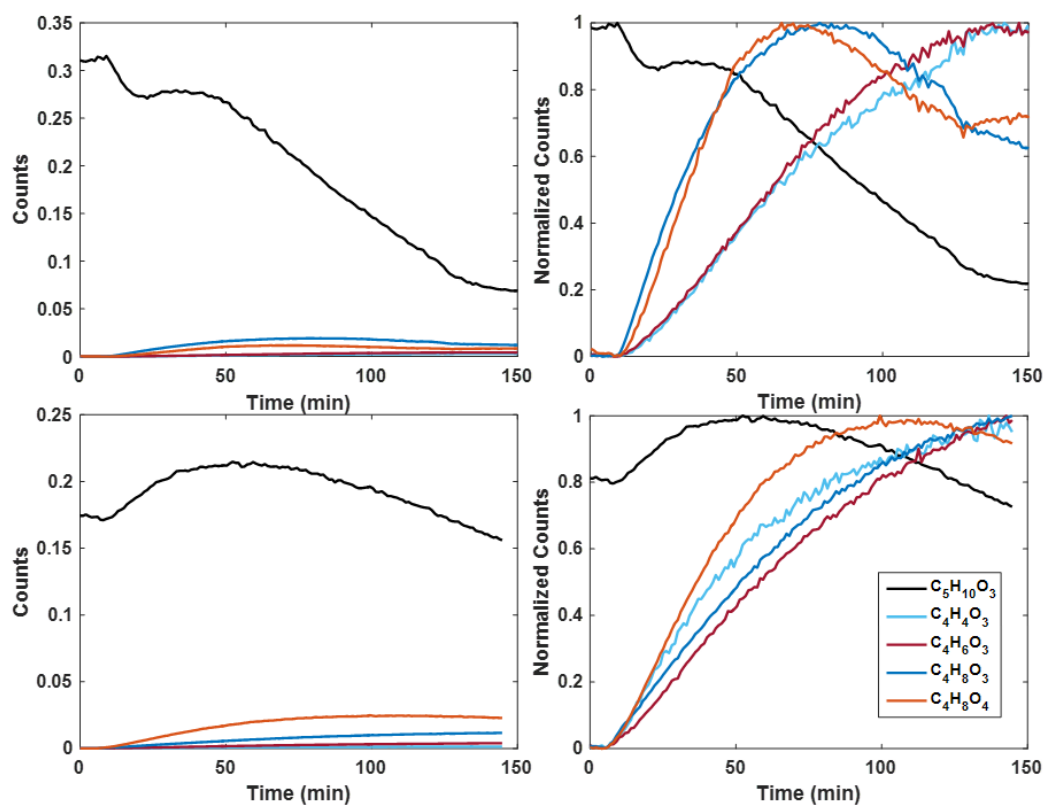


Figure 2.10: Traces of the four carbon products from the oxidation of 1,2-ISOPOOH (top) and 4,3-ISOPOOH (bottom). On the left are the observed counts and on the right there are the counts normalized to one. These compounds have several possible candidate molecular structures, so we will not suggest any one structure for them they may in fact be the sum of several isomers.

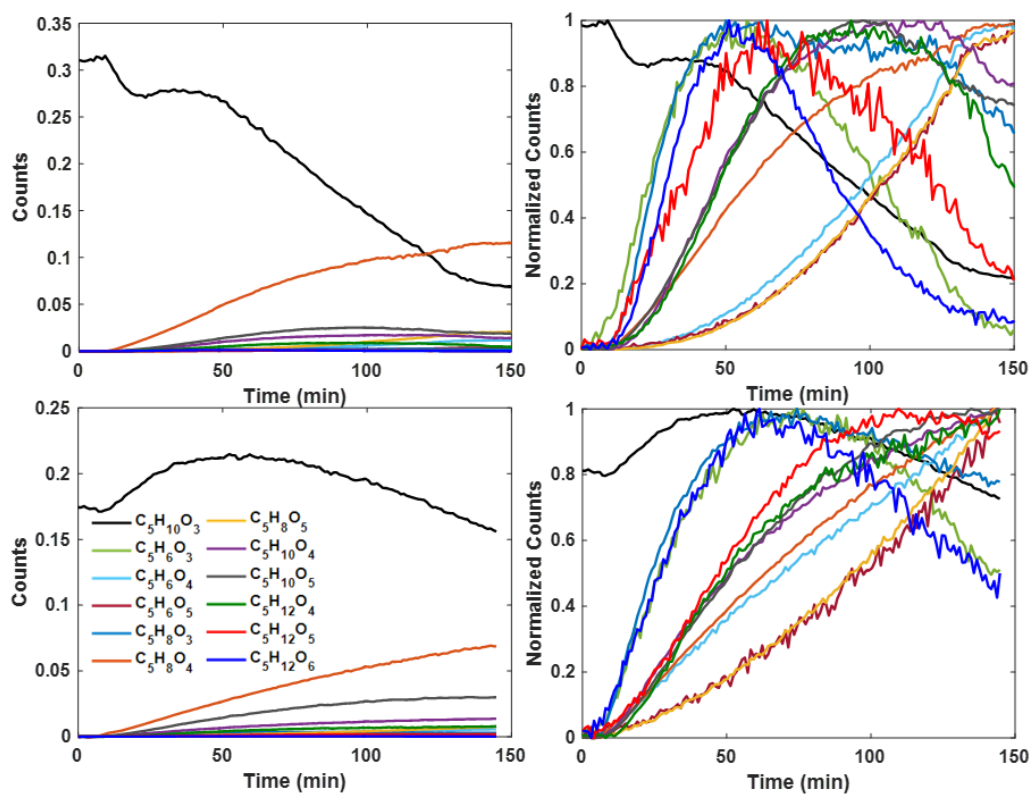


Figure 2.11: Traces of the five carbon products from the oxidation of 1,2-ISOPROOH (top) and 4,3-ISOPROOH (bottom). On the left are the observed counts and on the right, there are the counts normalized to one. These compounds have several possible candidate molecular structures so we will not suggest any one structure for them they may in fact be the sum of several isomers.

The product of $\text{RO}_2\text{-HO}_2$ chemistry is the recently reported isoprene dihydroxy dihydroperoxide ($\text{C}_5\text{H}_{12}\text{O}_6$).⁶¹ This product is observed as a primary product albeit with very small signal intensities. It is formed from ISOPOOH exclusively and has a fast loss rate. It is worth noting that the superoxide (O_2^-) radical anion reacts with RO_2 at a rate that is 100 times faster than HO_2 .⁷ With a pK_a of 4.88⁷ we expect most of the HO_2 to be present as O_2^- in the product experiments ($\text{pH} = 6$). This indicates that the RO_2 from ISOPOOH+OH effectively oxidizes O_2^- . $\text{C}_5\text{H}_{12}\text{O}_6$ is not observed during pH 4 experiments. This could be due to the lower reactivity of HO_2 towards RO_2 and/or to a hindered sensitivity. Standards of this compound are needed to test these hypotheses. There are many other compounds generated during the oxidation of ISOPOOH and later generation products but most of them have low signal intensities.

Oxidation of β -IEPOX in the aqueous phase seems to follow previously established mechanisms.^{5,4} β -IEPOX oxidation is much slower than that of ISOPOOH due to the lack of an OH addition pathway. OH reacts with IEPOX via hydrogen abstraction at either of the carbons bearing the alcohol groups or at the epoxide, with negligible contributions from attack to the methyl group.

Oxidation at the alcohol bearing carbons can lead to an aldehyde $\text{C}_5\text{H}_8\text{O}_3$ and subsequent oxidation of the aldehyde or its hydrate can lead to $\text{C}_5\text{H}_8\text{O}_4$. $\text{C}_5\text{H}_8\text{O}_4$ has the highest signal intensity at the end of the oxidation experiments for both ISOPOOH isomers implying a high yield or very high sensitivity. The kinetics of $\text{C}_5\text{H}_8\text{O}_4$ formation imply it is a first-generation product of IEPOX oxidation. This makes it unlikely that $\text{C}_5\text{H}_8\text{O}_4$ is formed via sequential oxidation of IEPOX and IEPOX aldehyde. A possible pathway for direct formation of $\text{C}_5\text{H}_8\text{O}_4$ from IEPOX is oxidation at the epoxide position followed by oxygen addition forming a $\text{C}_5\text{H}_9\text{O}_5$ peroxy radical. This peroxy radical can react with RO_2 to form a variety of products including a $\text{C}_5\text{H}_9\text{O}_4$ alkoxy radical that can isomerize and form $\text{C}_5\text{H}_8\text{O}_4$ (see figure 2.12 for a scheme). According to this mechanism, $\text{C}_5\text{H}_8\text{O}_4$ is an aldehyde and its oxidation should lead to a carboxylic acid $\text{C}_5\text{H}_8\text{O}_5$. $\text{C}_5\text{H}_8\text{O}_5$ is indeed the third-generation product with the most signal intensity at the end of our experiments. More experi-

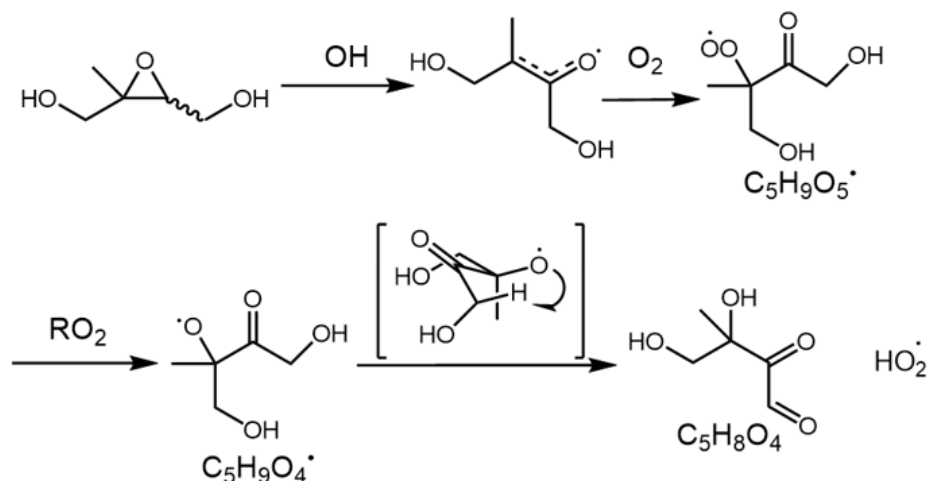


Figure 2.12: Possible formation mechanism for $C_5H_8O_4$ as a first-generation product from IEPOX.

ments are needed to identify the structure of $C_5H_8O_4$ and its contribution to aerosol formation.

Oxidation at the alcohol positions can also lead to a dihydroxycarbonyl ($C_4H_8O_3$), after intramolecular hydrogen shifts.⁵ Further oxidation of these leads to hydroxydicarbonyls ($C_4H_6O_3$), detected during the latter part of the oxidation experiments. C5-tetrols ($C_5H_{12}O_4$), products of IEPOX hydrolysis, are common tracers for IEPOX-SOA and were observed in small amounts. This is expected since at the acidities used during these experiments, hydrolysis contributes only a small amount to the loss of IEPOX.¹⁶ Attack at the epoxide position leads to a $C_5H_9O_5$ radical that, in addition to the chemistry mentioned previously, can react with HO_2 to form $C_5H_{10}O_5$. Although an isomer of this $C_5H_{10}O_5$ can form from ISOPOOH oxidation, the compounds growth curve suggests that production from IEPOX is the main formation pathway for $C_5H_{10}O_5$ (Figure 2.11). $C_5H_9O_5$ can also react with an RO_2 , which leads to a tertiary alkoxy radical that fragments to produce glycolic acid and hydroxyacetone. Oxidation of IEPOX also contributes to glyoxal and methylglyoxal as later generation oxidation products.

Products containing four carbons include $C_4H_6O_3$, $C_4H_8O_3$, $C_4H_8O_4$ and $C_4H_4O_3$. Out

of these products, $C_4H_8O_3$ and $C_4H_8O_4$ have the most signal. In the case of 1,2-ISOPPOOH, $C_4H_8O_3$ and $C_4H_8O_4$ appear to have a strong direct contribution from ISOPPOOH, with most of their production happening at the beginning of the experiment. $C_4H_8O_3$ has a stronger signal than $C_4H_8O_4$ by about a factor of 1.5. This ratio is reversed during the oxidation of 4,3-ISOPPOOH. $C_4H_8O_4$ has the highest signal out of the C_4 compounds and the ratio of $C_4H_8O_4$ to $C_4H_8O_3$ is about 2 at their peak intensity. The difference in the $C_4H_8O_3$ and $C_4H_8O_4$ ratio between the ISOPPOOH isomers could be because fragmentation and loss of the alcohol bearing carbon in 4,3-ISOPPOOH can lead to an aldehyde. This aldehyde can undergo a unimolecular isomerization reaction involving the aldehydic hydrogen.⁵⁸ The same fragmentation of 1,2-ISOPPOOH leads to a ketone which is less reactive and does not contribute additional isomerization pathways. This difference is also highlighted in the photolysis products section discussed below.

Formation of compounds with two or three carbons appears to be secondary as no oxidation products are formed directly from either ISOPPOOH isomer. I^- CIMS does not detect products with few oxygen-containing functional groups, such as those that may be formed from fragmentation of ISOPPOOH or IEPOX at the beginning of the experiment. The detected C_2 and C_3 compounds have three or more oxygens, suggesting that they are either fragmentation of highly oxidized C_5 or C_4 oxidation products or produced from the oxidation of previously formed, less oxidized, C_2 and C_3 compounds that could not be detected.

Direct photolysis of 4,3-ISOPPOOH contributes an additional branch of products. These products were observed with UV-B light in the presence of an OH trap and include formaldehyde ($HCHO$), formic acid (CH_2O_2), $C_2H_4O_3$. Although methacrolein is not observed, its oxidation product ($C_4H_8O_4$) is observed. $C_4H_8O_4$ is formed during 1,2-ISOPPOOH oxidation but not during its photolysis (Figures 2.10 and 2.13). The presence of $C_4H_8O_4$ during photolysis is unique to the 4,3-ISOPPOOH isomer. Solvent cage effects, where radical pair reacts with each other before diffusing and reacting with other compounds in solution (like benzoic acid) can explain these obser-

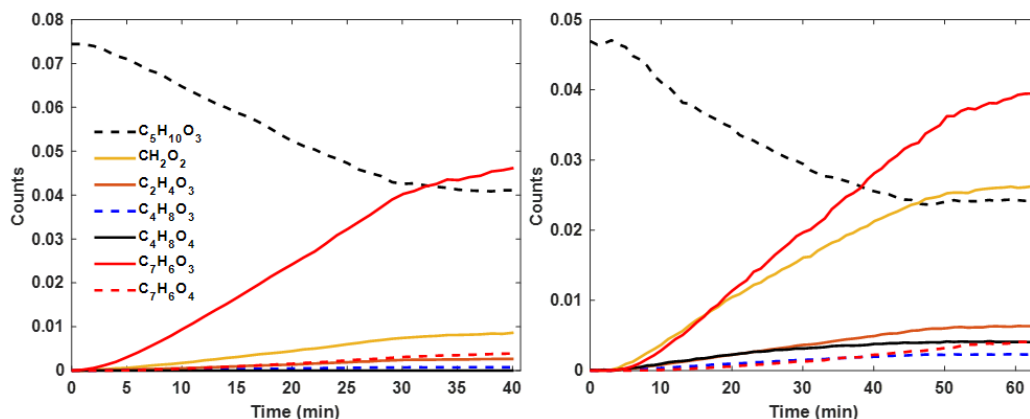


Figure 2.13: 254 nm photolysis products of 1,2-ISOPROOH (left) and 4,3-ISOPROOH. Formic acid and $C_4H_8O_4$ are markedly enhanced in the case of 4,3-ISOPROOH.

vations.

The $C_4H_8O_4$ product is either methacrolein hydroxyhydroperoxide or 2-methylglyceric acid. The peroxide could be formed via OH reaction with MACR in the solvent cage followed by addition of O_2 to form the $C_4H_7O_4$ peroxy radical and reaction with HO_2 . An isomerization reaction of the same RO_2 could lead to 2-methylglyceric acid after hydrolysis of the resulting epoxide.⁵⁸ The presence of an OH scavenger makes it unlikely that $C_4H_8O_4$ is the product of bimolecular radical chemistry (RO_2-HO_2), suggesting that this compound is indeed 2-methylglyceric acid. This also explains why $C_4H_8O_4$ is not observed for 1,2-ISOPROOH photolysis: the same isomerization pathway is not available for the equivalent MVK RO_2 . Formic acid and HCHO are formed at the same rates, implying that they are formed in the same reaction step and not sequentially.

2.7 OH PRODUCTION

Uptake of peroxides has been proposed as a possible source of OH in atmospheric waters.⁶⁸ Therefore, we designed experiments to determine the production of OH from ISOPROOH photolysis

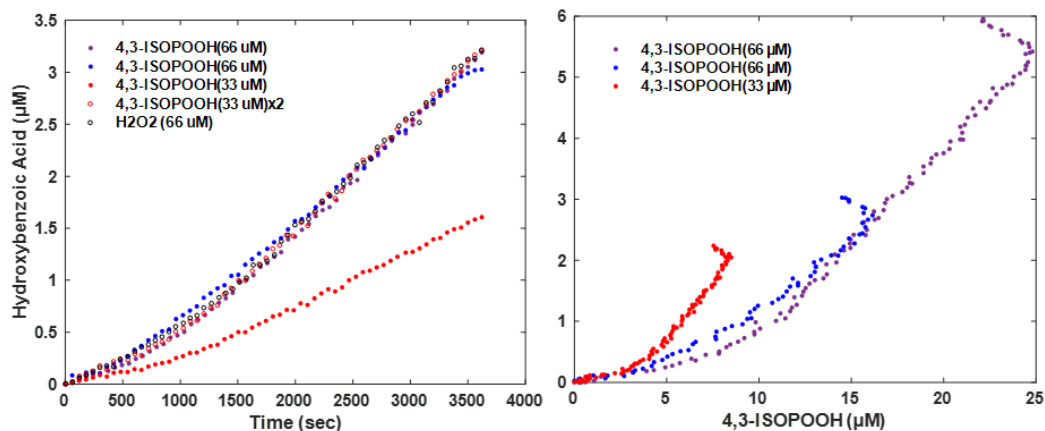


Figure 2.14: OH production experiments. A total of three experiments were carried out with initial 4,3-ISOPROOH concentrations of 66, 66 and 33 μM. Time trace of hydroxybenzoic acid production under UV-B illumination. (left) The 33 μM experiment was multiplied by 2 to show the linearity in OH production with concentration. Using H₂O₂ (66 μM) under the same conditions leads to the same amount of OH. A plot of hydroxybenzoic acid formation against 4,3-ISOPROOH decay (right) is non-linear under the detection conditions. This could be due to hysteresis in the hydroxybenzoic acid signal or interferences with the ISOPROOH signal.

under UV-B irradiation. A total of 4 experiments were performed: three using 4,3-ISOPROOH (66 μM, 66 μM and 33 μM) and, for comparison, an experiment using H₂O₂ (66 μM). The solutions contained 1 mM benzoic acid as an OH trap. The formation of hydroxybenzoic acid was used as a surrogate for OH production, corrected for its yield and isomer distribution.⁵⁹ Figure 2.14 shows the results from 4 experiments. OH production from ISOPROOH at a given concentration is essentially the same as that of H₂O₂. Using half of the ISOPROOH affords half of the OH as shown by the 33 μM experiment, which excludes other oxidation pathways or OH sources. MACR cannot be detected with the instrumentation available. However, as mentioned in the previous section, products of MACR oxidation such as C₄H₈O₄ and C₄H₈O₃ are observed. At the concentrations used during these experiments, MACR should not compete significantly with benzoic acid for OH radicals. This suggests that OH radicals react with MACR before leaving the solvent cage and reacting with benzoic acid.

2.8 AMS RESPONSE

During the product experiments, part of the output from the atomizer was directed towards an HR-ToF-AMS. Figures 2.15 and 2.16 show the data acquired from this instrument. ISOPOOH oxidation in the condensed phase leads to an enhancement in the Org/SO₄ ratio as ISOPOOH is converted to IEPOX and other compounds. The increase in Org/SO₄ is the fastest during ISOPOOH oxidation and slows, but continues to increase, when IEPOX is the main species in solution. IEPOX is measured to have a K_H value that is 2-3 orders of magnitude larger than ISOPOOH, so an increase in Org/SO₄ is consistent with this transformation.⁷⁷ The Org/SO₄ ratio eventually triples, suggesting that oxidation, even with a strong photolysis term (254 nm light), leads to a decrease in the volatility of the organics in solution. Oxygen to carbon (O:C) ratios increase very rapidly from 0.4 to 0.6 and then continue to increase slowly to 1. The fast increase at the beginning is due to the ISOPOOH to IEPOX reaction. The hydroperoxide group likely fragments during electron impact ionization leading to an underestimation of the O:C ratio of ISOPOOH and other organic hydroperoxides in AMS data. IEPOX is a much more stable isomer of C₅H₁₀O₃ whose O:C ratio is then correctly measured. Continued oxidation of IEPOX leads to an eventual increase in O:C ratios up to about 1, while H:C ratios drop from 2 to 1.8.

AMS data from the oxidation experiments were analyzed by Positive Matrix Factorization (PMF). Results are shown in figure 2.16. Experiments afford a three-factor solution, which can be associated to generations of oxidation products: initial ISOPOOH (factor 1), IEPOX and other first-generation products (factor 2), and later generation products (factor 3). The mass spectra of the associated PMF factors became more fragmented as the experiment proceeds, as expected for a higher degree of oxidation. Factor 2 correlates with m/z 82, a mass commonly used as a tracer of IEPOX SOA. For 1,2-ISOPOOH m/z 82 is enhanced along with factor 2 and then decays as the experiment progresses and IEPOX is oxidized. In the case of 4,3-ISOPOOH m/z 82 is enhanced

and stays elevated even after continued oxidation. This data suggests that m/z 82 is not enhanced by aqueous-phase oxidation of IEPOX since the same IEPOX isomer is formed during oxidation of 1,2 and 4,3-ISOPROOH. The data implies instead that other ISOPROOH oxidation products can contribute significantly to m/z 82.

Bypassing the diffusion drier allows more water to remain in the particles before detection by the AMS. This increases the fraction of organics that remains in the particle phase but does not lead to differences in the observed mass spectrum and elemental ratios. The total amount of organics in this type of aerosol is limited by the amount of water in them. The amount of water in aerosols is controlled by the relative humidity and concentrations of inorganics like sulfuric acid. Reductions in SO_2 emissions can affect secondary organic aerosol concentrations directly by removing sulfuric acid (reducing IEPOX uptake) and indirectly by removing water to which organics can partition into.^{47,9}

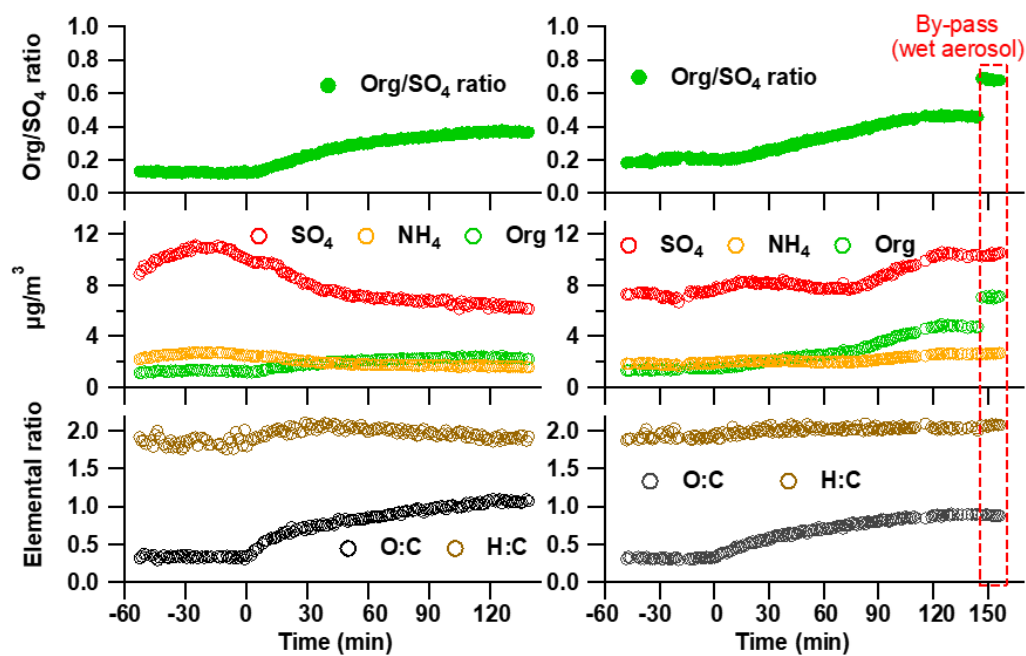


Figure 2.15: AMS results from aqueous oxidation of 1,2-ISOPROOH (left) and 4,3-ISOPROOH (right). Both experiments share similar trends in their organic to sulfate, oxygen to carbon and hydrogen to carbon ratios.

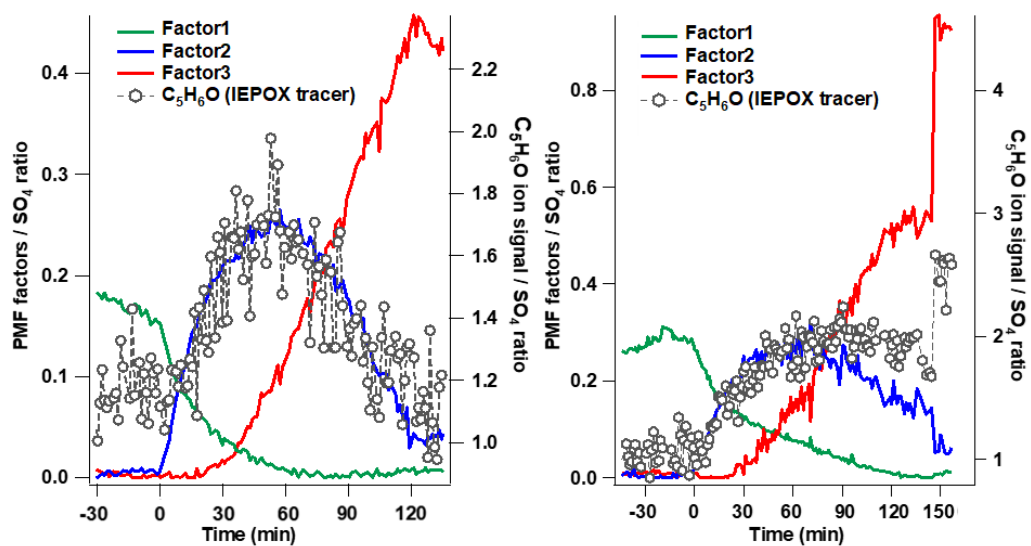


Figure 2.16: Positive Matrix Factorization affords a three-factor solution for both experiments. These factors account for the initial ISOPOOH (factor 1), a factor for first generation products (factor 2) and a factor for later generation products (factor 3). Factor 2 correlates strongly with the C_5H_6O ion signal which has been shown to be enhanced in IEPOX SOA.

2.9 IMPLICATIONS

This work provides insights into many aspects of the aqueous-phase chemistry of ISOPOOH. Measured Henry's Law constants were large and likely lead to significant partitioning of ISOPOOH into clouds or fog. Gas-phase concentrations of ISOPOOH of 1 ppb would lead to a 100 μM concentration in water, which is close to the concentrations used in our experiments. Henry's law constants differed by a factor of ten between the isomers. This difference could not be captured by models. Oxidation of ISOPOOH in the aqueous phase leads to IEPOX and other low-volatility products that have been shown to contribute to secondary organic aerosol in previous gas phase experiments.^{61,70} A comparison between glyoxal and ISOPOOH (Figure 2.17) provides context to these results. ISOPOOH's abundance, reaction rate with OH, Henry's law constants, and production of species previously found in aerosol suggests a large contribution to SOA via aqueous processing if the same is true for glyoxal, which is still an open question. ISOPOOHs can partition effectively into water, are sources of OH, have fast reaction rates with OH and their oxidation leads to products that contribute to aerosol mass. Due to the poor solubility of NO, oxidation in the condensed phase is likely to lead to an enhancement in low-NO_x oxidation products even in the presence of anthropogenic influence. Oxidation in the condensed phase leads to an increase in the organic content of aerosol generated from an ISOPOOH solution. Although we observed the formation of fragmentation products, the organic to sulfate ratio in particles generated from these solutions continued to increase monotonically as oxidation proceeded. IEPOX formation was correlated with enhancements in m/z 82 as shown previously. 82 m/z decreased with IEPOX oxidation in the case of 1,2-ISOPOOH but stayed elevated during 4,3-ISOPOOH oxidation, even after IEPOX was oxidized. Since 1,2-ISOPOOH is the main isomer with respect to abundance and K_H , we expect 82 m/z to be diminished in aged IEPOX aerosol or after significant aqueous processing. In addition, AMS data shows an underpredicted O:C ratio when ISOPOOH is the main species in solution.

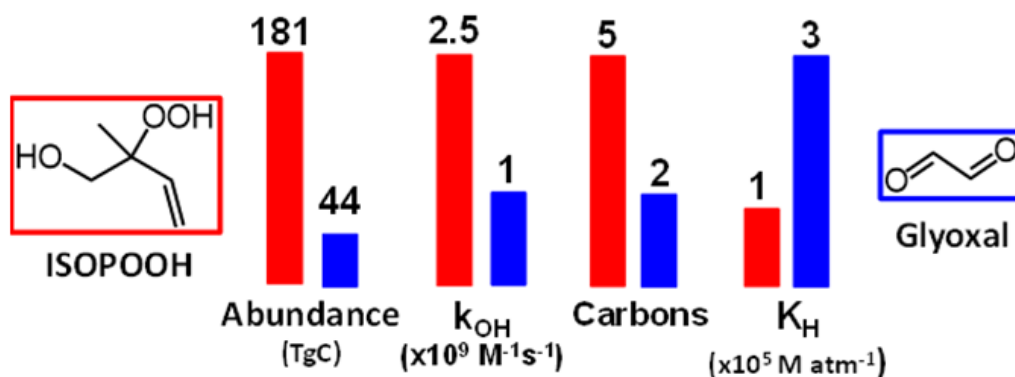


Figure 2.17: Both ISOPOOH and glyoxal can undergo aqueous-phase processing. ISOPOOH is produced in much larger amounts and has a faster reaction rate in the aqueous phase which accounts for the smaller Henry's Law constant. This implies that if glyoxal oxidation in the aqueous-phase is important, ISOPOOH oxidation is likely to be significant as well.

This is corrected when ISOPOOH is oxidized into IEPOX. We suggest that organic hydroperoxide O:C ratios are not well captured by AMS instrumentation. Additional experiments are needed to confirm this hypothesis.

The observed products (figures 2.7-2.11) suggest that oxidation in the condensed phase follows similar mechanisms as in the gas phase. The hydroxyl radical (OH) reacts with organic molecules, either by addition or hydrogen abstraction, resulting in an organic radical (R). Oxygen adds to these radicals forming peroxy radicals (RO_2) that can react with other RO_2 , the hydroperoxy radical (HO_2) or undergo isomerization. However, there are key differences in the oxidation mechanisms in the condensed phase: concentrations depend on solubility, diffusion rates are much slower and thermalization is much faster. Solvent cage effects also affect the way in which radicals behave, increasing the rate of radical recombination and altering fragmentation patterns. The photolysis products of 4,3-ISOPOOH are good examples of this effect. In addition, while the oxidation of aldehydes often leads to fragmentation and release of CO or CO_2 in the gas phase,¹³ the same process often leads to carboxylic acids in the condensed phase. The large number of C5 compounds observed in these

experiments showcase this reduced tendency to fragment during oxidation. The increased functionalization at the expense of fragmentation found in aqueous phase oxidation preserves the carbon skeleton of the initial VOC, reduces the product's volatility and increases the compound's solubility leading to additional aqSOA mass after the water evaporates. Fragmentation, when it occurs, leads to volatile compounds when the number of carbons lost is one. Since fragmentation occurs later in the oxidation, C₂ and higher fragmentation products are likely highly oxidized aldehydes, alcohols and organic acids, which can remain in the condensed phase or participate in accretion reactions. This is consistent with the observed products and AMS behavior. Future work should explore the effects of this chemistry using climate models.

3

The isoprene low- NO_x oxidation pathway

3.1 ABSTRACT

Considerable uncertainty remains in the oxidation of isoprene under low- NO_x conditions. The relative importance of RO_2 reactions with NO , HO_2 and unimolecular isomerization is key to understand this process. The yields of formaldehyde and glyoxal from the oxidation of isoprene low NO_x products have not been measured, preventing the establishment of unambiguous oxidation pathways. In this work, we perform gas-phase photooxidation experiments with standards of ISOPOOH , IEPOX and isoprene under a variety of NO_x conditions. We use the yields of formaldehyde and glyoxal along with measurements of NO and oxygenated VOCs to modify the Master Chemical Mechanism (MCM) so it can account for the observed products under all experimen-

tal conditions. Our experimental and modeled results suggest that glyoxal to formaldehyde ratios (RGF) are a good indicator of RO_2 fate, but uncertainty in the efficiency of $\text{RO}_2 + \text{HO}_2$ reactions can hinder the usefulness of this measure. Finally, part of the changes made to the MCM were included in the GEOS-Chem model, allowing us to discuss the effects of this chemistry in a global scale.

3.2 INTRODUCTION

ISOPRENE IS THE MOST WIDELY emitted biogenic volatile organic compound (BVOC) in the world.⁴¹ It is released into the atmosphere by deciduous trees and has a strong, temperature and light dependent diurnal cycle. It dominates atmospheric chemistry in many regions in the world due to its rapid reaction with the hydroxyl radical (OH) and abundance. Isoprene oxidation products can also contribute to secondary organic aerosol which impacts climate⁹⁷ and human health.⁹² For these reasons, understanding the atmospheric degradation of isoprene and its oxidation products is essential to global models of atmospheric composition.

The reaction of isoprene with OH proceeds via addition to carbons 1 or 4 and leads to two main allylic radicals. Oxygen addition to these radicals can lead to two β -hydroxy peroxy radicals and to four δ -hydroxy peroxy radicals. The fate of these peroxy radicals is modulated by their bimolecular reaction rates.¹⁰¹ Reaction with the hydroperoxyl (HO_2) or nitrogen oxides (NO_x) can lead to organic peroxides or organic nitrates and carbonyls respectively. Isomerization reactions can also occur and are particularly important to the δ - isomers.^{105,18} The chemistry of the main products in high NO_x environments is well understood due to their commercial availability and stability.^{83,18,64}

In remote locations where NO_x mixing ratios are low, the main products of isoprene oxidation are isoprene hydroxy hydroperoxides (ISOPOOH). These compounds have been shown to react

with OH to form isoprene epoxy diols (IEPOX), recycling OH.⁸¹ These epoxides can undergo reactive uptake onto acidic aerosols and can contribute significantly to secondary organic aerosol.^{36,69,77} In addition, the fraction of ISOPOOH that does not make IEPOX corresponds to highly oxygenated compounds that directly contribute to secondary organic aerosol (SOA) due to their low volatility.^{70,61}

In recent years, the availability of synthetic pathways for ISOPOOH and IEPOX has increased our knowledge of the atmospheric role of these compounds. Studies have addressed their contributions to secondary organic aerosol, their oxidative stress potential (biological),⁶⁰ and interferences in their measurements.^{86,71} Studies investigating the products of ISOPOOH and IEPOX oxidation show a complex degradation pathway that is highly dependent on NO_x concentrations.^{95,5,4} Isomerization reactions have been shown to contribute to the oxidation of these compounds, in many cases with OH recycling.²⁴

Many compounds are generated during isoprene oxidation. The yields of formaldehyde (HCHO) and glyoxal (CHOCHO) are of interest because these compounds can be observed from satellites.^{72,74} Due to their short lifetimes, HCHO and CHOCHO are tracers of photochemistry occurring at a particular location. The ratio between CHOCHO and HCHO has been suggested as tool to diagnose anthropogenic influence in remote environments. Previous work has studied direct glyoxal production from isoprene but uncertainty remains under low-NO_x conditions.³⁵ Understanding their production and fate can increase the utility of these measurements, providing constraints on oxidant levels, VOC emissions and potentially SOA formation on a global scale.²⁸ Previous ISOPOOH and IEPOX oxidation experiments lacked the necessary instrumentation to measure the yields of HCHO and glyoxal. Since these compounds are expected as co-products, establishing unambiguous oxidation mechanisms becomes a challenge.

In this study, we performed several oxidation experiments in an environmental chamber with isoprene, and several isomers of ISOPOOH and IEPOX under a variety of NO_x conditions. The

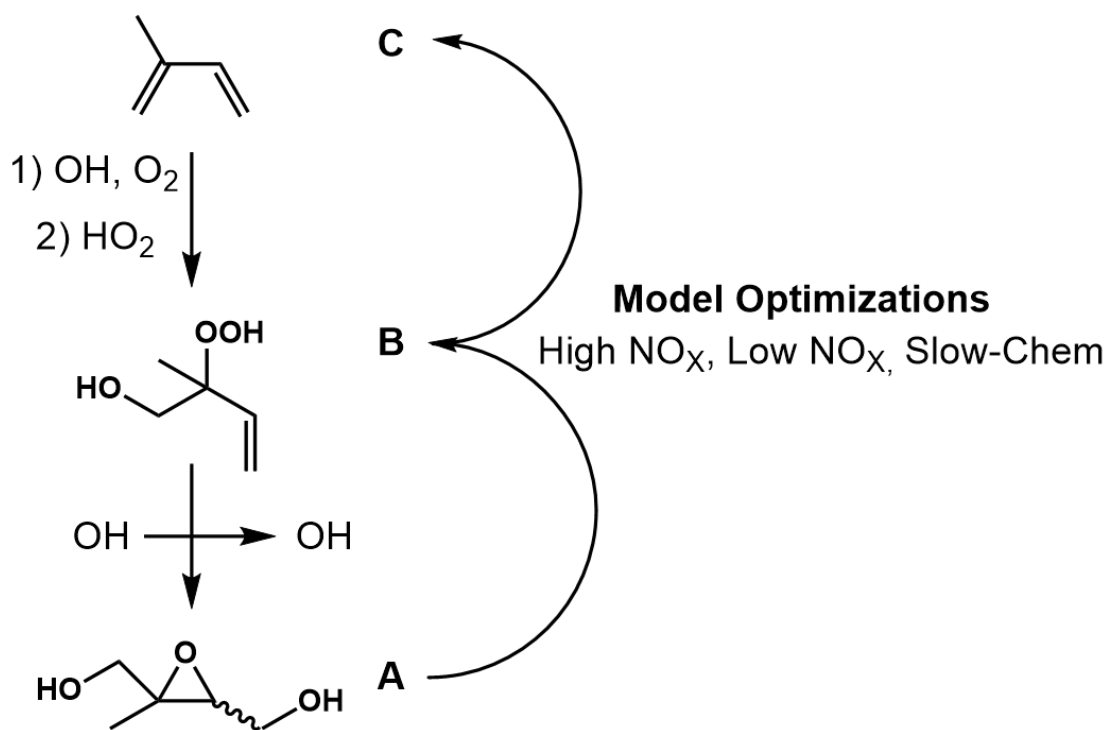


Figure 3.1: Under low-NO_x conditions isoprene oxidation leads to ISOPOOH and in an additional oxidation step, IEPOX. The MCM was optimized to fit the results of our experiments starting from the bottom-up. A) The oxidation of IEPOX was improved and those changes included when modeling B) ISOPOOH and C) isoprene. This was performed with the high-NO_x experiments and repeated for the low-NO_x and slow-chem experiments.

experiments were designed to understand the products of both the bimolecular reactions with NO and HO₂ and unimolecular isomerization reactions. The results from these experiments were modeled using the Master Chemical Mechanism (v3.3.1).⁵³ Figure 3.1 shows our approach to analyze these experiments. The oxidation of IEPOX, ISOPOOH and isoprene was optimized sequentially, starting from IEPOX and including those changes to optimize ISOPOOH followed by isoprene. Using these measurements we provide an updated version of the MCM isoprene chemistry that is self-consistent with the experiments we performed.

3.3 EXPERIMENTAL METHODS

Isoprene was measured using a gas chromatograph with a flame ionization detector (GC-FID). Oxidized volatile organic compounds (OVOC) were measured using a chemical ionization mass spectrometer (CIMS), employing CF_3O^- as the reagent ion.¹⁹ CF_3O^- CIMS is sensitive to many OVOCs including ISOPOOH, IEPOX, hydroxyacetone, glycolaldehyde, isoprene nitrates, 2,3-dihydroxy-2-methylpropanal, and 2-hydroxy-3-oxobutanol. HCHO was measured via laser induced fluorescence using the NASA ISAF instrument.¹² Glyoxal was measured using laser induced phosphorescence using the Madison Laser Induced Phosphorescence instrument (Mad-LIP) instrument.⁴⁹ NO was measured using the NCAR Chemiluminescence instrument.⁸⁵ The CIMS sampled continuously throughout the experiments. The formaldehyde, glyoxal and NO instruments had prohibitively large sampling rates and had to sample at specific intervals.

Experiments were performed in two 1 m³ Teflon-FEP chambers which have been described previously.^{83,5,4} Table 3.1 is a list of experiments performed in this work. The chamber is illuminated using UV lights (Sylvania 350 blacklights). Low NO_x experiments were performed by using H₂O₂ as the OH source. The desired VOC was then added, and the lights turned on. High NO_x experiments were performed in a similar manner but including the addition of NO.

“Slow-chem” experiments were designed to extend peroxy radical lifetimes and investigate isomerization reactions. The source of OH in the slow-chem experiments was photolysis of isopropyl nitrite. Isopropyl nitrite photolyzes into isopropyl alkoxy radical and NO. The alkoxy radical decomposes into acetone and HO₂. HO₂ and NO react creating OH and NO₂. In these experiments we assumed that the photolysis cross-section of isopropyl nitrite was the same as the one for methyl nitrite. High NO_x and slow-chem experiments were performed in a different bag from the low NO_x experiments to keep NO_x backgrounds low. For the slow-chem experiments, the lamps were covered, and only indirect irradiation could reach the chamber. The chambers were flushed with

clean air several times in between experiments. Background experiments were performed routinely to characterize background production of several species. This was only significant for HCHO, primarily under high NO_X conditions. HCHO was plotted twice, a trace was the measured concentration and another trace had the expected contribution from background production removed.

1,2-ISOPROOH, 4,3-ISOPROOH were synthesized as described in chapter 2. trans-IEPOX and cis-IEPOX were synthesized according to previously published procedures.⁴ These compounds were added to the chamber by blowing clean air over a drop of the purified product. The vapors were added until the desired concentration was reached. H_2O_2 was added in the same manner using a drop of 30% H_2O_2 in water. Isoprene and NO were added to the chamber by filling a 500 cm^3 bulb which was then transferred into the chamber.

The experiments were modeled using the Framework for 0-D Atmospheric Modeling (F0AM).¹⁰⁶ The Master Chemical Mechanism (MCM v 3.3.1) was used to simulate the experiments.⁵³ The model was initialized to the observed values at the time the lights were turned on. The light spectrum (included in F0AM) was scaled by 5.17 to match the experimentally observed photolysis rate of glyoxal. All radical species were unconstrained except for one experiment (high NO_X cis-IEPOX) where OH was held constant. The model ran on a 60 second time interval where lights were indicated to be on or off. The irradiation for the slow-chem experiments was scaled to match the level of oxidation we observed. In all figures, the MCM 3.3.1 model results are shown as solid lines and the model with changes made in this work are shown as dashed lines.

Experiment List			
Date	Exp	Compound	Conditions
9/27/2015	1	Blank	High NO _x
9/27/2015	2	1,2 ISOPOOH	High NO _x
9/28/2015	3	Blank	Low NO _x
9/28/2015	4	1,2 ISOPOOH	Low NO _x
9/28/2015	5	4,3 ISOPOOH	Low NO _x
9/29/2015	6	4,3-ISOPOOH	High NO _x
9/29/2015	7	trans-IEPOX	High NO _x
9/30/2015	8	cis-IEPOX	High NO _x
9/30/2015	9	trans-IEPOX	High NO _x
10/1/2015	10	trans-IEPOX	Low NO _x
10/1/2015	11	cis-IEPOX	Low NO _x
10/2/2015	12	1,2 ISOPOOH	Slow-Chem
10/3/2015	13	Blank	Slow-Chem
10/4/2015	14	1,2 ISOPOOH	Slow-Chem (HT)
10/5/2015	15	trans-IEPOX	Slow-Chem
10/6/2015	16	Blank	High NO _x
10/6/2015	17	Isoprene	High NO _x
10/7/2015	18	Isoprene	Slow Chem
10/8/2015	19	Isoprene	Slow Chem (HT)
10/9/2015	20	Isoprene	Low NO _x
10/10/2015	21	Glyoxal	Photolysis
10/14/2015	22	Glycolaldehyde	High NO _x

Table 3.1: Experiments performed in this work. HT = high temperature

3.4 RESULTS

3.4.1 HIGH NO_x EXPERIMENTS

The high NO_x experiments provide information on peroxy radical branching ratios. The high NO levels used during these experiments make reaction with NO the only possible fate of the RO₂ radicals generated by the reaction of OH and VOCs. The RO₂ lifetime in these experiments is shorter than 0.02 s. Barring organic nitrate formation, these reactions lead to the corresponding alkoxy rad-

icals (RO) which will then undergo either decompositions that lead to stable products or hydrogen abstraction from nearby hydroperoxide hydrogens, generating a new RO₂ radical. The decomposition of alkoxy radicals has been studied in relatively simple systems.² However, their decomposition in highly oxygenated carbon skeletons is uncertain.

In this study we use the observed products of IEPOX, ISOPOOH and isoprene oxidation under high NO_x conditions to make assumptions about: 1) initial peroxy radical distributions and b) the fate of alkoxy radicals. This is important for the ISOPOOH and IEPOX experiments where the formation of RO₂ radicals is not expected to be reversible. The isoprene generated RO₂ radicals are allylic in nature. This makes the O₂ addition step reversible and their fate depends on bimolecular reaction rates and unimolecular isomerization processes. A large portion of these were experimentally determined recently and their results are incorporated into this work.¹⁰¹

IEPOX

The MCM oxidation scheme of IEPOX is shown in figure 3.2. Reaction with OH leads to 5 main products: two aldehydes and three peroxy radicals. Under these experimental conditions the peroxy radicals (C₅₈AO₂, C₅₉O₂ and C₅₇O₂) react with NO to produce the alkoxy radicals C₅₈AO, C₅₉O and C₅₇O and NO₂. These fragment into two products with either 4 and 1 carbons or 2 and 3 carbons as shown in figure 3.3. The four carbon products are 2,3-oxobutanol, 2,3-hydroxy-2-methylpropanal, 2-hydroxy-3-oxobutanol. The last two are referred to as C₄ diols since they are structural isomers and the CIMS cannot tell them apart. Carbon monoxide and formaldehyde accompany the 4 carbon products. The other fragmentation pattern leads to 3 carbon products methylglyoxal and hydroxyacetone which have glyoxal, glycolaldehyde and the glycolaldehyde acyl peroxy radical as co-products. Previous experiments lacked measurements of HCHO and glyoxal. This limits the ability to constrain the yields of each individual pathway since some products can be formed from multiple pathways as shown in figure 3.3.

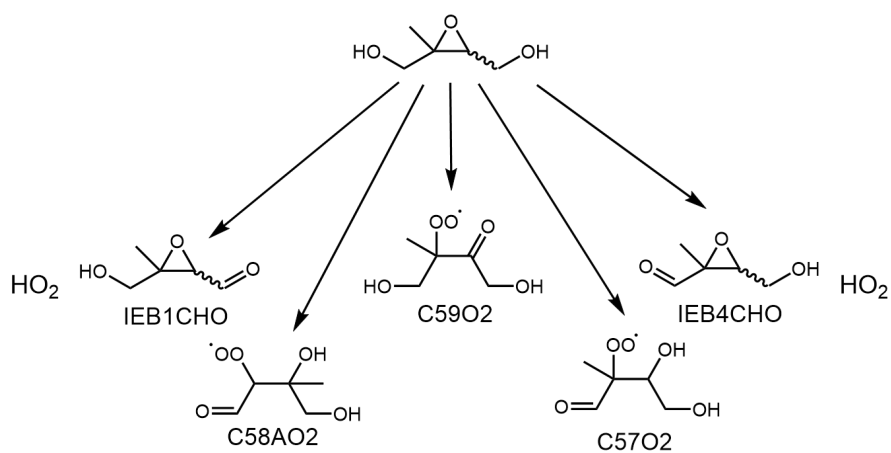


Figure 3.2: The MCM 3.3.1 IEPOX oxidation scheme. This scheme is based on the Bates et al. paper on IEPOX oxidation.⁴ OH reacts by abstracting a hydrogen from the carbons bearing the alcohol groups or from the epoxide hydrogen. Reaction at the alcohols can lead to IEPOX aldehydes (IEB1CHO, IEB4CHO) or to the C58AO2 and C57O2 RO₂ radicals. Reaction at the epoxide hydrogen leads to the C59O2 radical. Reaction at the methyl hydrogens is negligible. Table 3.2 summarizes their respective yields.

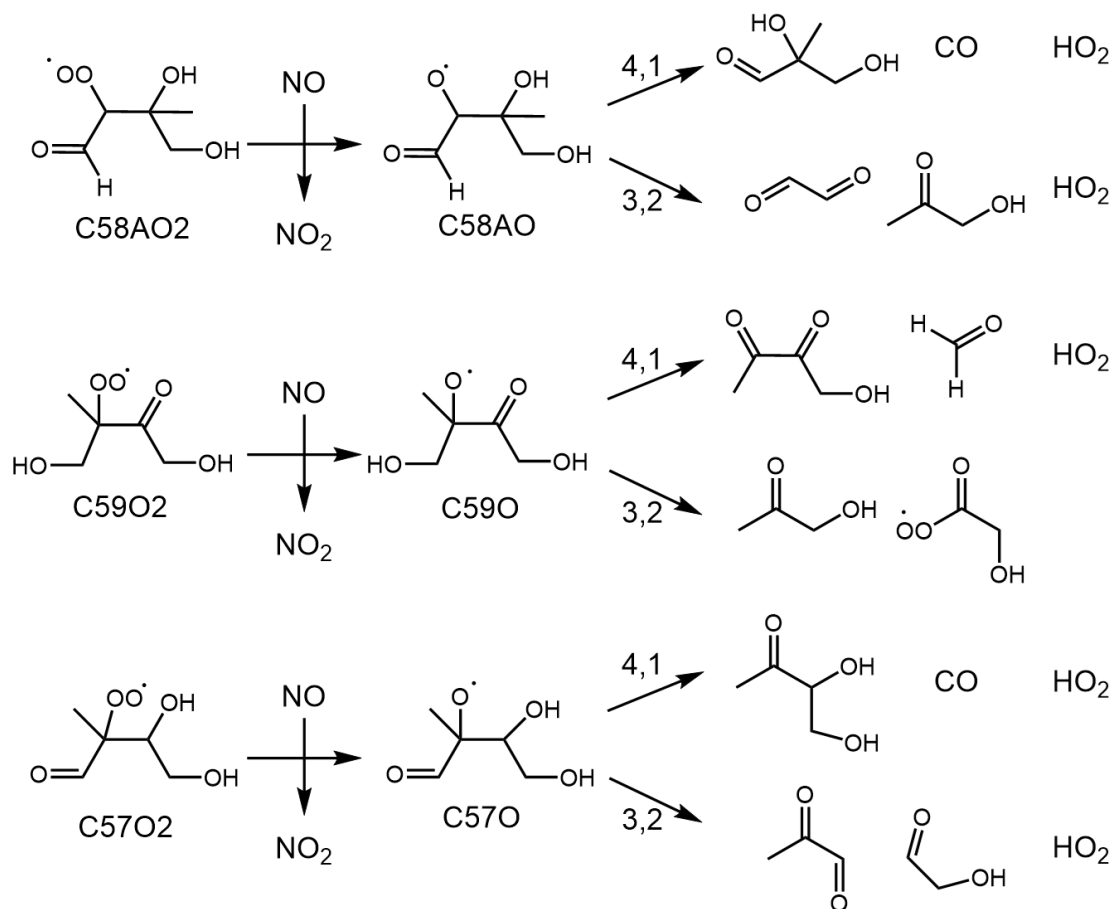


Figure 3.3: Fate of the IEPOX RO₂ radicals. Reaction with NO leads to the corresponding alkoxy radicals. These have two main fragmentation patterns a) 4 and 1 or b) 3 and 2 carbon products. Only C59O₂ leads to HCHO under this oxidation scheme. Since many compounds have co-products the observed yields constrain both the initial RO₂ concentrations and the fragmentation patterns of the alkoxy radicals. HO₂ and NO₂ are co-products of all reaction paths except C59O.

The high NO_x experiments were modeled using the MCM v3.3.1. The model results for the IEPOX experiments are plotted along with the experimental data in figures 3.4-3.6. The model run using the MCM, oxidizes too much IEPOX, overpredicts most of the observed products and has no production of C4 diols. Figures 3.5 also shows the results using an updated model using the changes described in table 3.2 and 3.3. In the MCM, cis- and trans-IEPOX, are represented as only one molecule (IEPOXB). This updated model separates IEPOXB into the cis and trans (cIEPOXB and tIEPOXB) isomers and uses the experimentally determined OH reaction rates for each of them. In order to fit the observed products the branching ratios for the initial product distribution had to be changed, increasing the yield of IEPOX aldehydes and lowering the yields of C58AO2 and C57O2, favoring the formation of C59O2. This is required to explain the large yield of formaldehyde observed during our experiments.

IEPOX first generation product distribution			
	MCM v3.3.1	This Work	
Species	IEPOX	cis	trans
C58AO2	37%	8%	13%
C59O2	15%	43%	27%
C57O2	37%	14%	19%
IEB1CHO	5.5%	20%	20.5%
IEB4CHO	5.5%	15%	20.5%

Table 3.2: Product distribution of the OH + IEPOX reaction. The MCM v3.3.1 distribution does not match the observations made during our chamber experiments.

cis-IEPOX was oxidized in a similar manner. The results are shown in figure 3.6. A C4 diol impurity was present during this experiment, its identity is unknown. The nature of this impurity

IEPOX Alkoxy Radical Fragmentation Pattern				
	MCM v3.3.1		This Work	
Radical	4,1	3,2	4,1 (c/t)	3,2 (c/t)
C58AO	0%	100%	55%	45%
C59O	0%	100%	80%	20%
C57O	0%	100%	20%/40%	80%/60%

Table 3.3: IEPOX alkoxy radical fragmentation. The values from this work are used to match the products observed during the chamber experiments.

can significantly alter the model results for C4 diol production. Additionally, the oxidation of cis-IEPOX cannot be captured by the model without constraining OH. There seems to be significant OH recycling under high- NO_x conditions in the oxidation of cis-IEPOX, which we cannot explain. As is the case for trans-IEPOX, the MCM overestimates glyoxal, hydroxyacetone and glycolaldehyde. There is no production of C4 diols and formaldehyde is underpredicted. An even larger yield of C59O2 is required to explain the formaldehyde formed during the oxidation of cis-IEPOX. The yield of formaldehyde from C59O during high NO_x oxidation is equal to the yield of C59O2 since the glycolic peroxyacyl radical reacts with NO and decomposes to CO_2 , HO_2 and HCHO.

Our results show clearly that the RO_2s formed from IEPOX oxidation lead to alkoxy radicals that have more than one fragmentation pattern. All three alkoxy radicals require fragmentation into 4,1 and 3,2 carbon products to reproduce the observed product yields. Furthermore, the measurements of glyoxal limit the amount of hydroxyacetone that can be formed from the C58AO2 radical pathway. This implies that formation of C59O2 is likely one of the major pathways for IEPOX oxidation, controlling the yields of both HCHO and hydroxyacetone. The previously observed ratio between aldehyde and ketone C4 diols is maintained in this work with the ketone having a significantly larger yield. In order for the model to match the experimental results we suggest that the C57O alkoxy radical fragmentation is treated differently between cis and trans IEPOX. This is due primarily to the large difference in the glycolaldehyde yield observed between these isomers. With

these branching ratios, and considering the relative abundance between trans and cis isomers, the direct yield of glyoxal under high NO_x conditions would be 5.1%. There is a possibility that isobaric impurities are contributing to the observed IEPOX signal. If that is the case the yields of the peroxy radicals determined in this work would be a lower limit.

Nitrate formation from the main IEPOX RO_2 s is expected to be small and was not included in this work. The products observed in these experiments imply large IEPOX aldehyde yields of 35% and 41% for cis and trans IEPOX respectively. It is unclear how these compounds will be oxidized in the atmosphere and if their contribution to aerosol is like that of IEPOX. The current MCM representation of IEPOX aldehyde (IEB1CHO, IEB4CHO) oxidation leads to glyoxal and methylglyoxal. However, the abstraction of the aldehyde hydrogen should be an important contributor to IEPOX aldehyde oxidation and it is not represented in the MCM. Standards of these compounds are needed to calibrate instruments and determine their atmospheric fate.

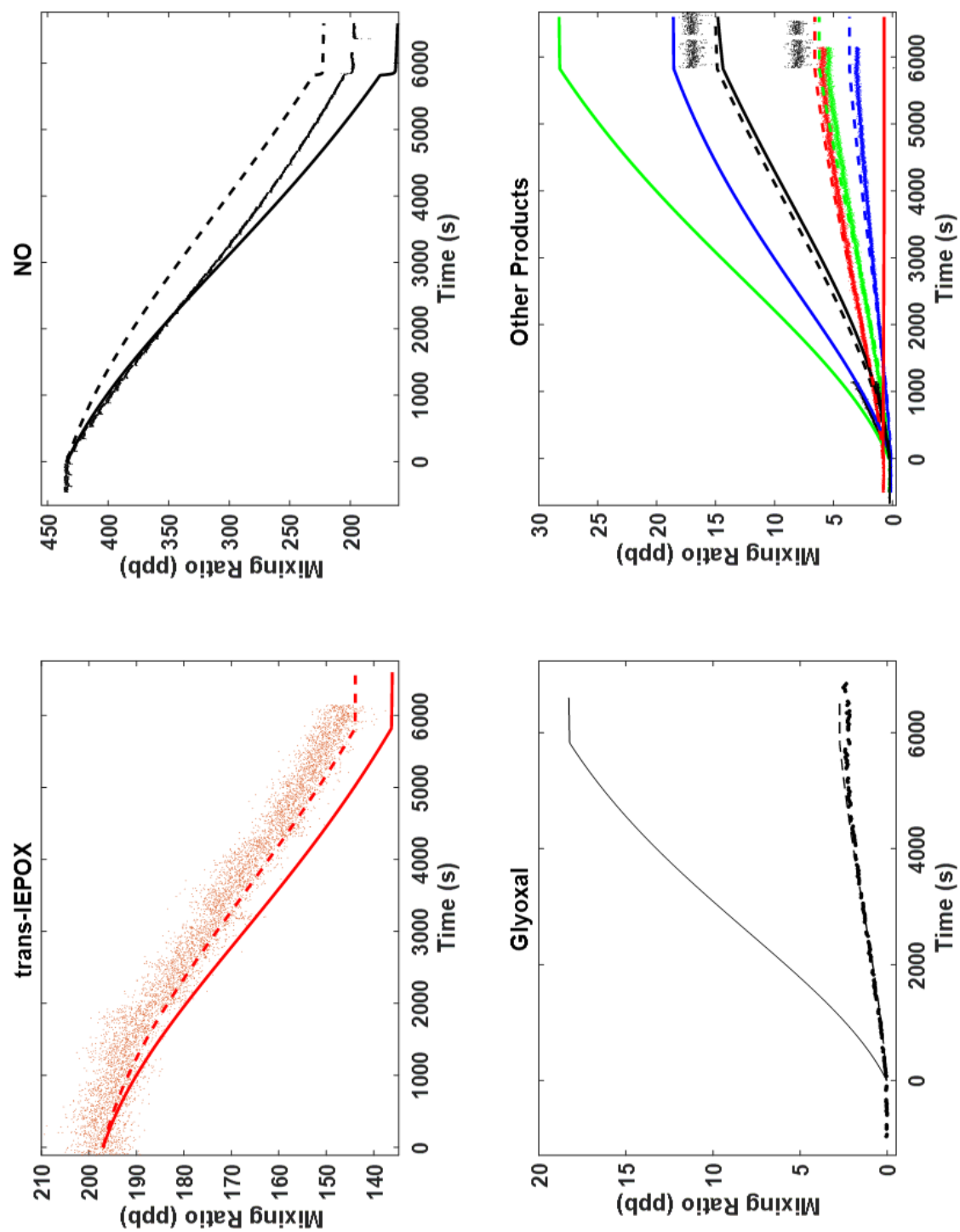


Figure 3.4: trans-IEPOX High NO_x oxidation. Solid lines are the MCM simulation, dashed lines include the changes made in this work. Other Products are formaldehyde (black), C4Diols (red), hydroxyacetone (green) and glycolaldehyde (blue).

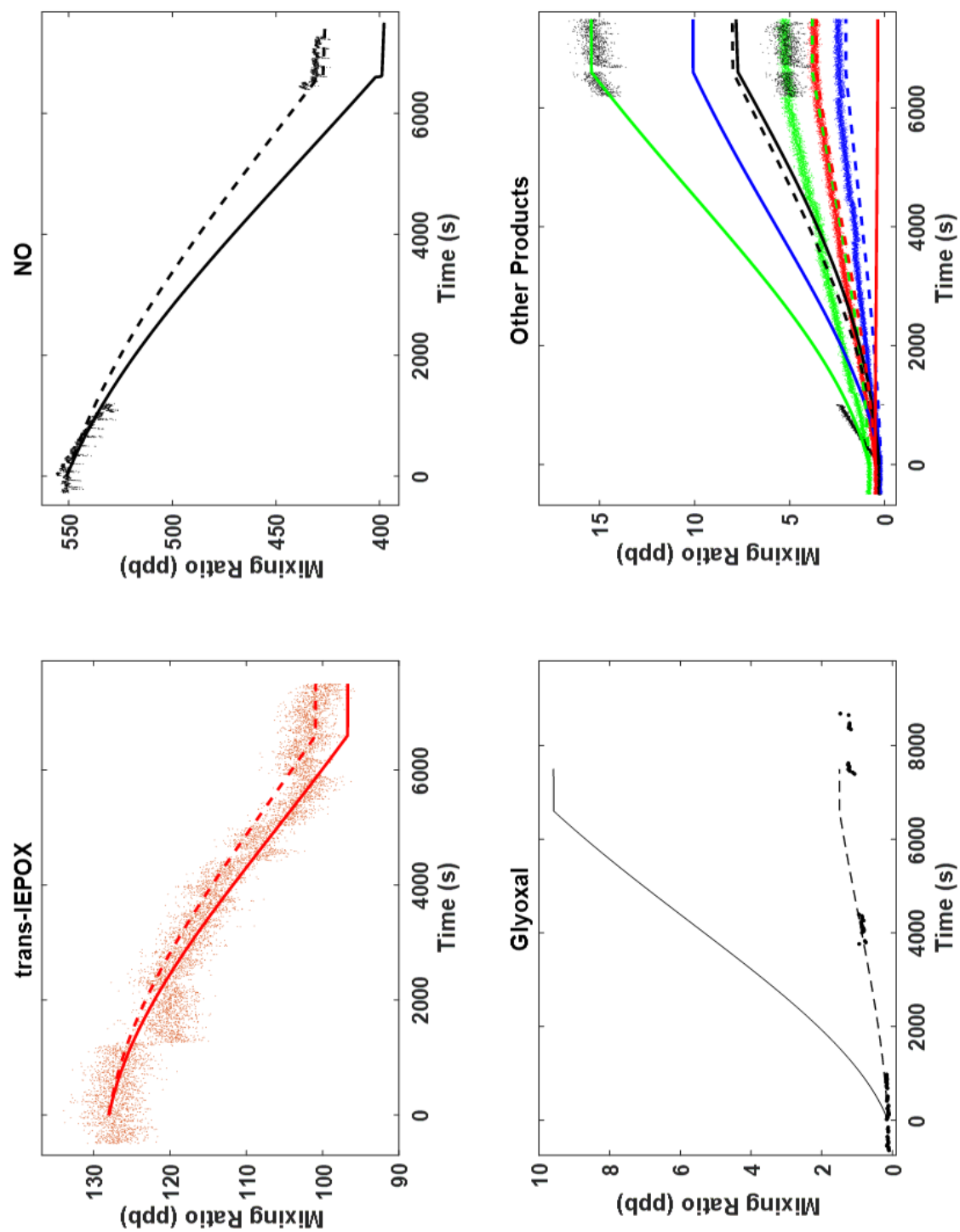


Figure 3.5: trans-IEPOX High NO_x oxidation 2. Other Products are formaldehyde (black), C4Diols (red), hydroxyacetone (green) and glycolaldehyde (blue). Solid line = MCM Dashed line = This Work

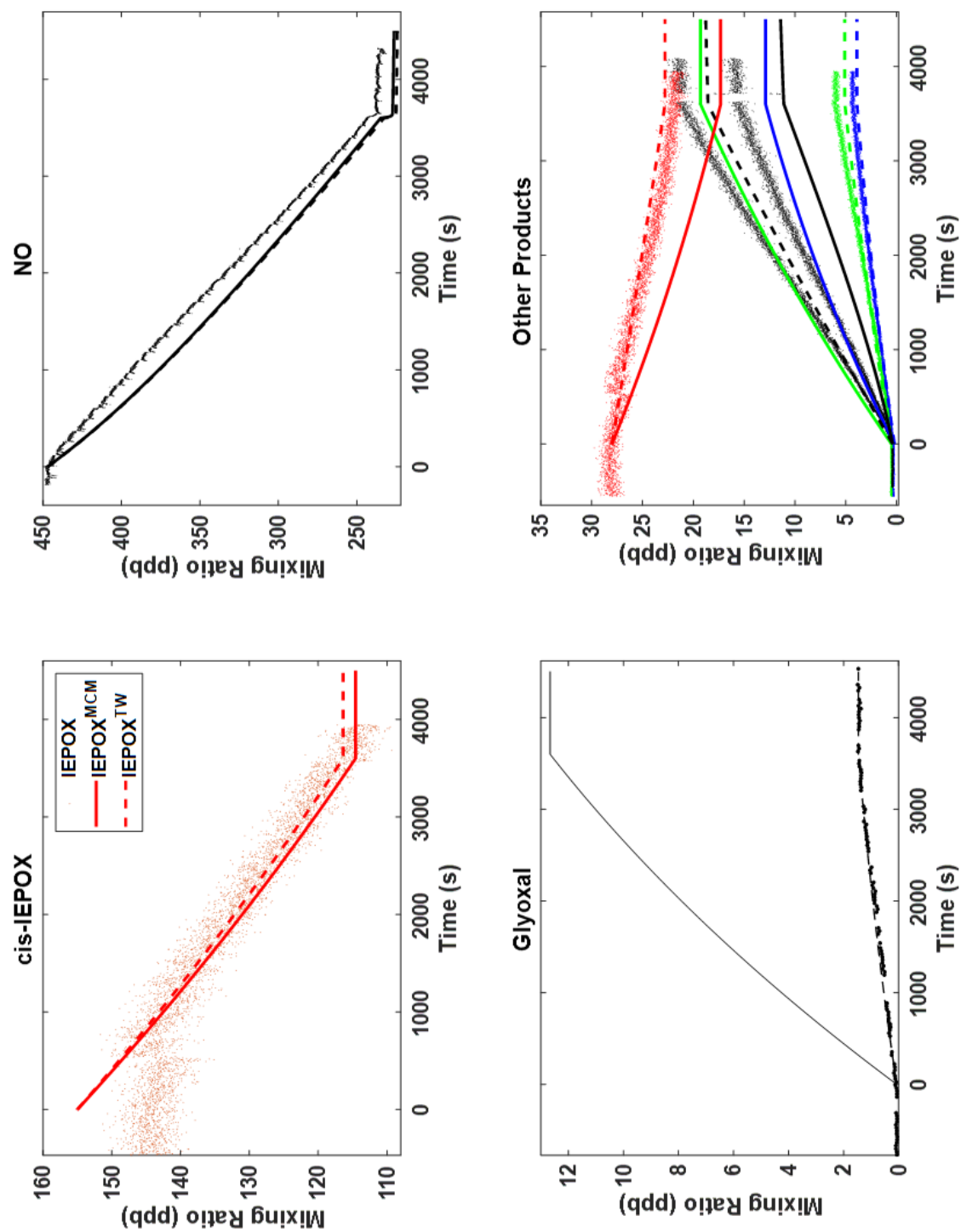


Figure 3.6: cis-IEPOX High NO_x oxidation. Other Products are formaldehyde (black), C4Diols (red), hydroxyacetone (green) and glycolaldehyde (blue). Solid line = MCM Dashed line = This Work

ISOPOOH

We performed high- NO_x experiments with 1,2- and 4,3-ISOPOOH. The MCM nomenclature for these isomers is ISOPBOOH and ISOPDOOH respectively. As is the case for IEPOX, the high NO_x experiments provide information on initial peroxy radical distributions and products. Figure 3.7 shows the MCM OH oxidation scheme for both ISOPOOH isomers. The formation of ISOPBOOHO₂ and ISOPDOOHO₂ was added in this work to account for the products observed during our experiments.

Table 3.4 features the branching ratios from the MCM and the ratios determined in this work. Since the compounds are isomers their oxidation scheme is similar. The secondary nature of the peroxide on ISOPDOOH allows for the formation of a hydroxy carbonyl compound 3-methyl-2-oxobut-3-enol known as HCOC5 in the MCM. Upon reacting with OH, HCOC5 is expected to form the C₅O₂ peroxy radical discussed in the IEPOX section which was determined to lead to formaldehyde and hydroxyacetone under these conditions.

Branching ratios of the ISOPOOH + OH reaction				
	MCM v3.3.1		This Work	
Species	ISOPBOOH	ISOPDOOH	ISOPBOOH	ISOPDOOH
IEPOXB	92%	75%	74%*	68%*
ISOPD(B)O ₂	8%	3%	11%	4%
ISOPD(B)OOHO ₂	N/A	N/A	15%	18%
HCOC5	N/A	22%	N/A	10%

Table 3.4: Branching ratios for ISOPOOH + OH. The MCM does not feature an OH addition pathway. In this work IEPOXB is divided into cis and trans isomers cIEPOXB and tIEPOXB. They are produced in a 1:2 cis:trans ratio as suggested by Bates et al.⁴

Recent literature shows that OH addition products like isoprene dihydroxy dihydroperoxides (C₅H₁₂O₆) are produced during the oxidation of ISOPOOH.^{61,23} As shown in figure 3.8 and 3.9,

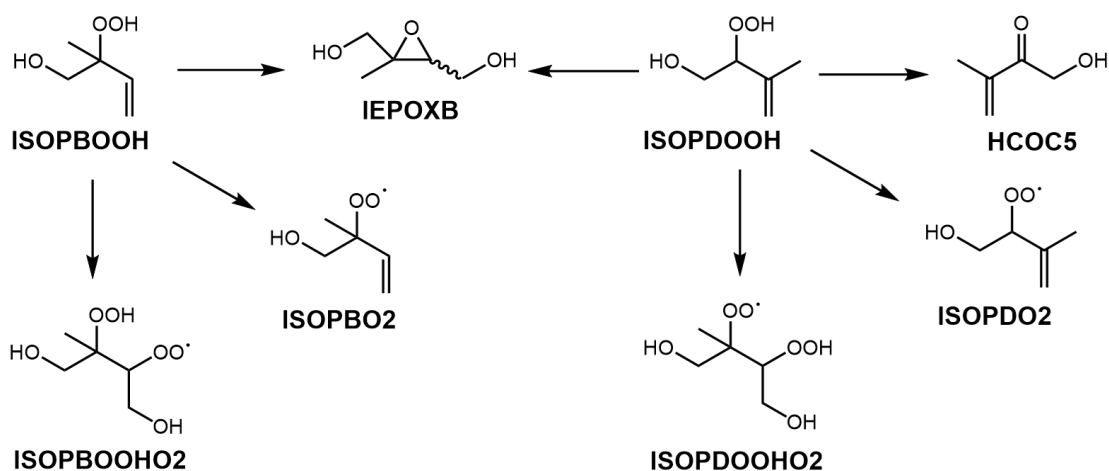


Figure 3.7: Oxidation scheme for the main ISOPROOH isomers. The MCM does not feature an OH addition pathway for these compounds so ISOPBOOHO2 and ISOPDOOHO2 were added in this work.

the oxidation of ISOPROOH has a direct yield of C4 diols. These compounds can only be produced by the OH addition channel. We propose an oxidation mechanism that allows for the formation of C4 diols under high- NO_X conditions and also accounts for the observed levels of hydroxyacetone and glycolaldehyde. This mechanism features OH addition to form the ISOPB(D)OOHO2 peroxy radical. Under high NO_X conditions, after reaction with NO, the corresponding alkoxy radical ISOPB(D)OOHO can fragment into HCHO and a C4 hydroxy hydroperoxide or undergo a hydrogen transfer from the hydroperoxide group to form a new RO_2 (ISOPB(D)OOHOHO2) radical. This step is necessary for the formation of C4 diols directly from ISOPROOH. This radical can then react with NO and fragment into 3 and 2 carbon or 4 and 1 carbon products in a manner similar to the IEPOX RO_2 radicals. These mechanisms are shown in figures 3.10 and 3.11 for 1,2-ISOPROOH and 4,3-ISOPROOH.

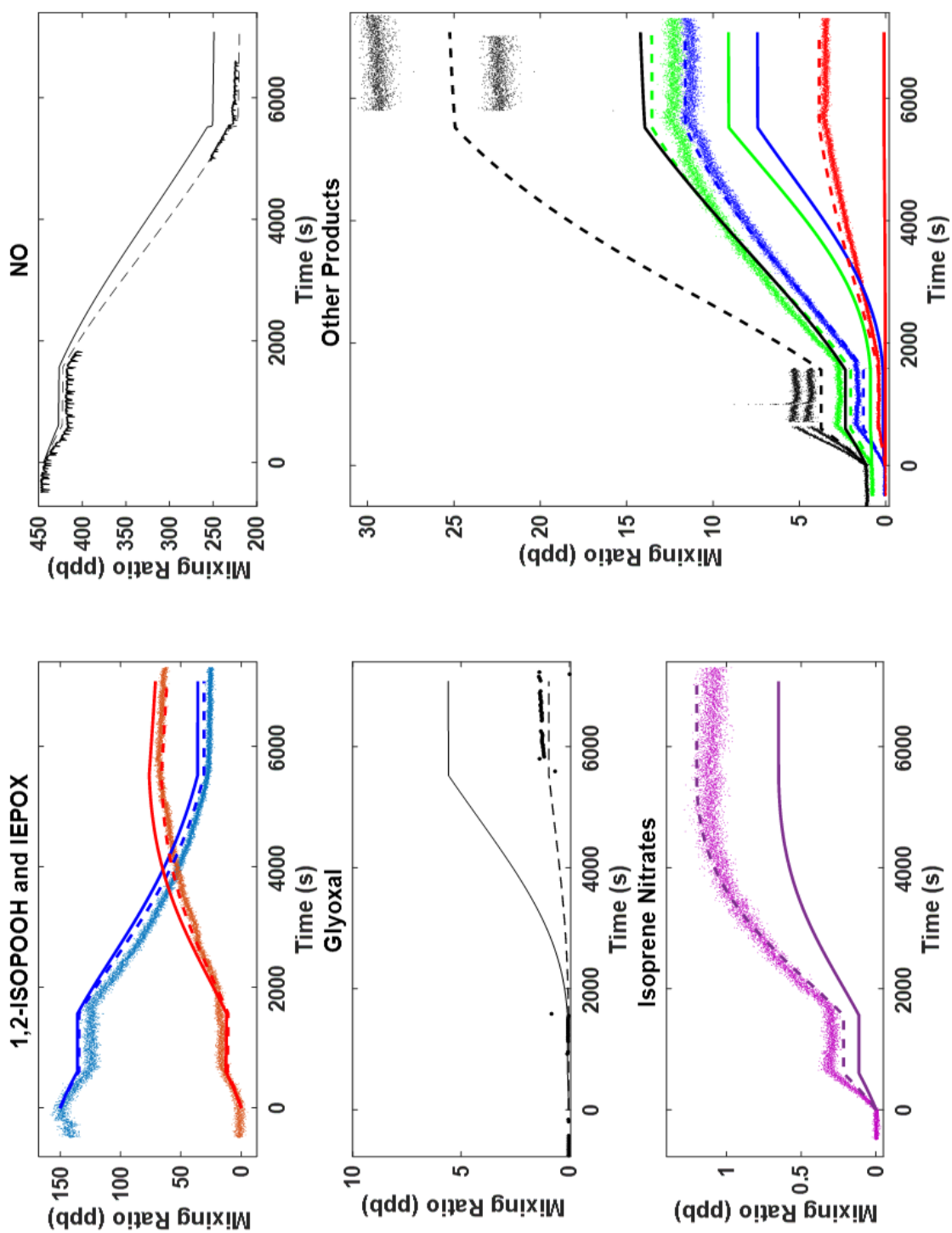


Figure 3.8: 1,2-ISOPOOH (light blue) High NO_x oxidation. Plotted products are IEPOX (orange), formaldehyde (black), C4Diols (red), hydroxyacetone (green) and glycolaldehyde (blue). Solid line = MCM Dashed line = This Work

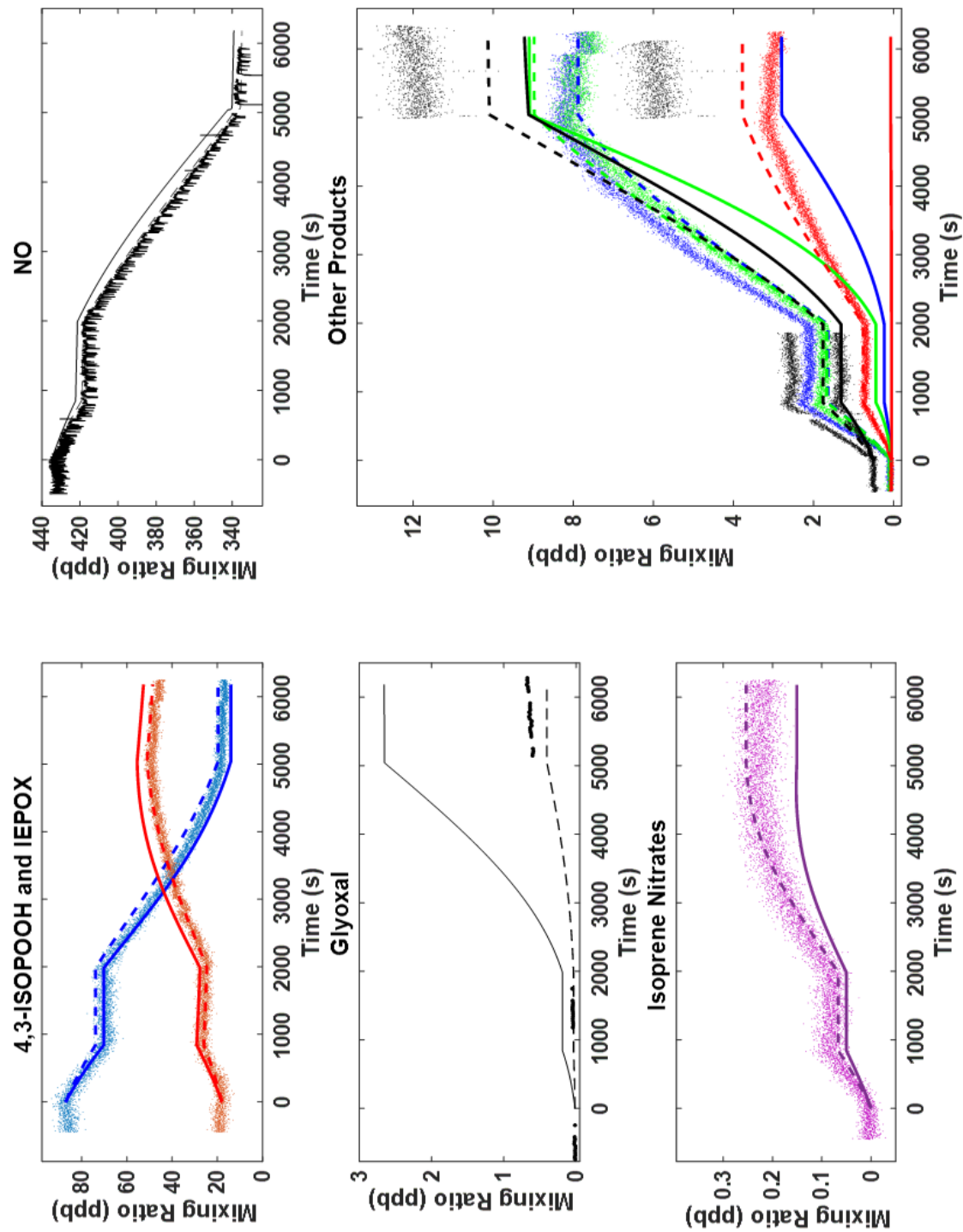


Figure 3.9: 4,3-ISOPOOH (light blue) High NO_x oxidation. Plotted products are IEPOX (orange), formaldehyde (black), C4Diols (red), hydroxyacetone (green) and glycolaldehyde (blue). Solid line = MCM Dashed line = This Work

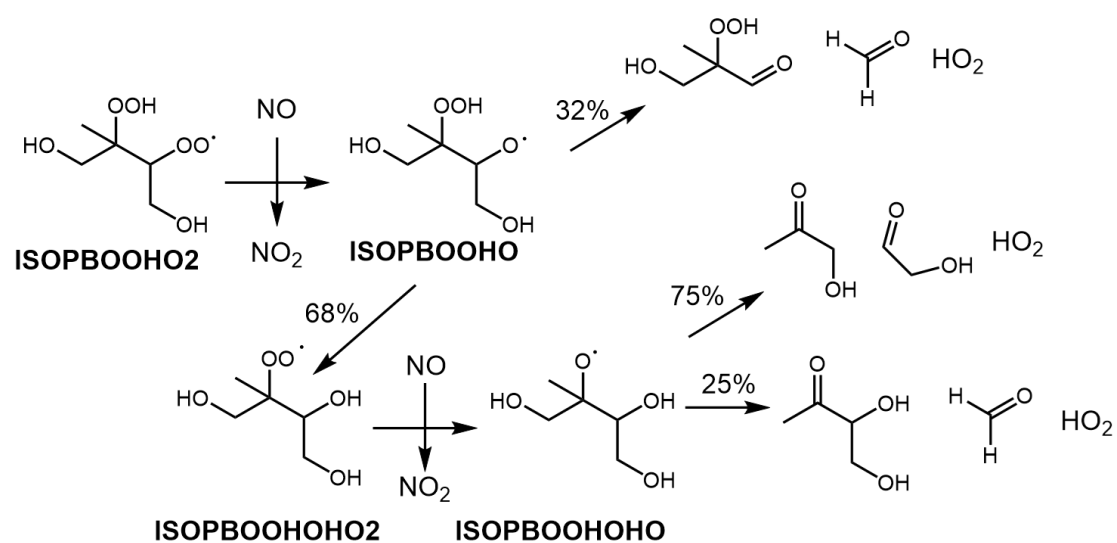


Figure 3.10: Suggested mechanism for the ISOPBOOH O₂ addition pathway. Branching shown was used in the model results shown in figure 3.7.

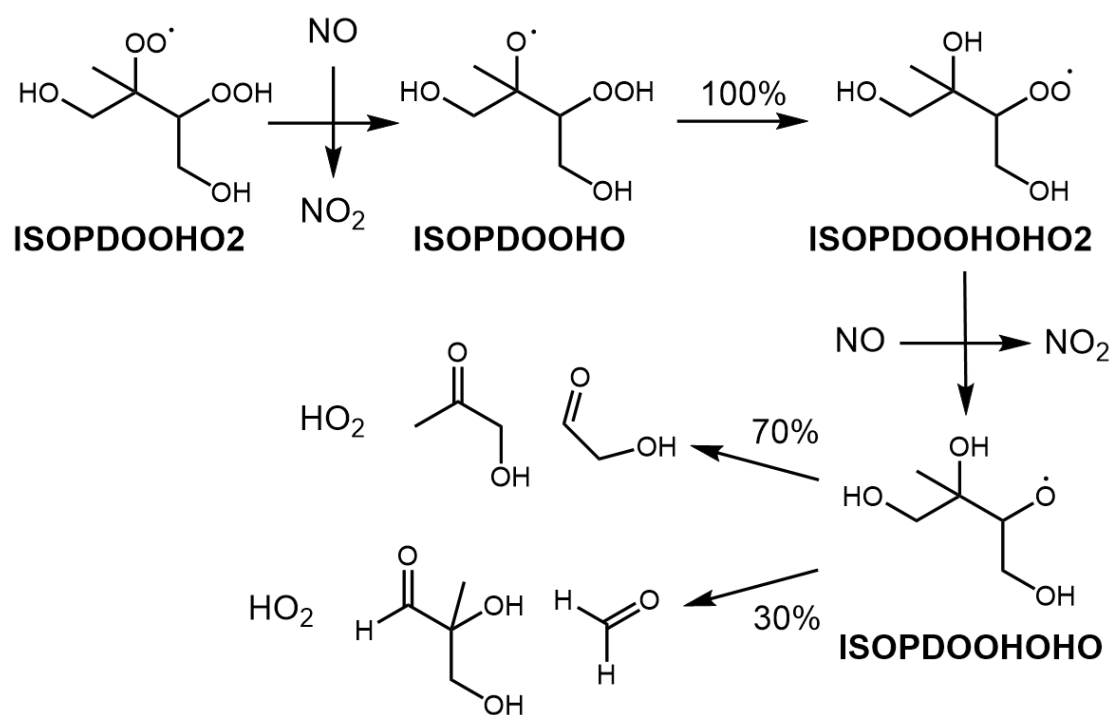


Figure 3.11: Suggested mechanism for the ISOPDOOH O₂ addition pathway. Branching shown was used in the model results shown in figure 3.8.

Abstraction of the peroxide hydrogen leads to the respective isoprene peroxy radical. Due to the reversibility of O_2 addition this can lead to scrambling of the β - and δ - isomers if the bimolecular reaction rates are low enough. This is not the case during the high NO_x experiments. Reaction with NO leads to MACR/MVK and HCHO and organic nitrates. The formation of organic nitrates from ISOP OOH is underpredicted in the MCM and well captured in this work after adjusting the yield to 13%.

ISOPRENE

The main products of isoprene high NO_x experiments are MACR/MVK, HCHO and isoprene nitrates. Since most of the changes in this work are around ISOP OOH and IEPOX they have limited effect in this experiment.

We updated the MCM isoprene chemistry using the recently published rates for isoprene peroxy radical dynamics and an organic nitrate yield of 13% for the first generation isoprene peroxy radicals (ISOPAO2, CISOPAO2, ISOPBO2, ISOPCO2, CISOPCO2, ISOPDO2). These changes capture nitrate formation very well as shown in figure 3.12. Formaldehyde is also well predicted by the model, which implies a good ratio between β and δ peroxy radicals. The MCM overpredicts glyoxal quite significantly. Primary production of glyoxal from isoprene under these experimental conditions happens via the C527O alkoxy radical. This is a product of the cis-4,1 peroxy radical, whose isomerization yields C527O2 and its reaction with NO leads to C527O. We adjusted the branching ratios of the decomposition of C527O slightly, to match our glyoxal observations. However, to account for C4 diol formation from isoprene we changed the decomposition of C526O2 and C527O2 to allow for the formation of C57O2 and C58AO2 as shown in figure 3.13. This also contributed to the reduction of the total glyoxal yield from isoprene in our simulation. The proposed hydrogen shifts are supported by recent work suggesting scrambling of peroxy radicals in RO_2 molecules that contain hydroperoxides.⁵⁴ Essentially, C526O2 and C527O2 are in equi-

librium with C526O2b and C527O2b, if the “b” version reacts with NO it leads to C57O2 and C58AO2. These changes in addition to the reduced yield of glyoxal from C527O lead to a better model agreement between the model and observations of glyoxal and C4 Diols.

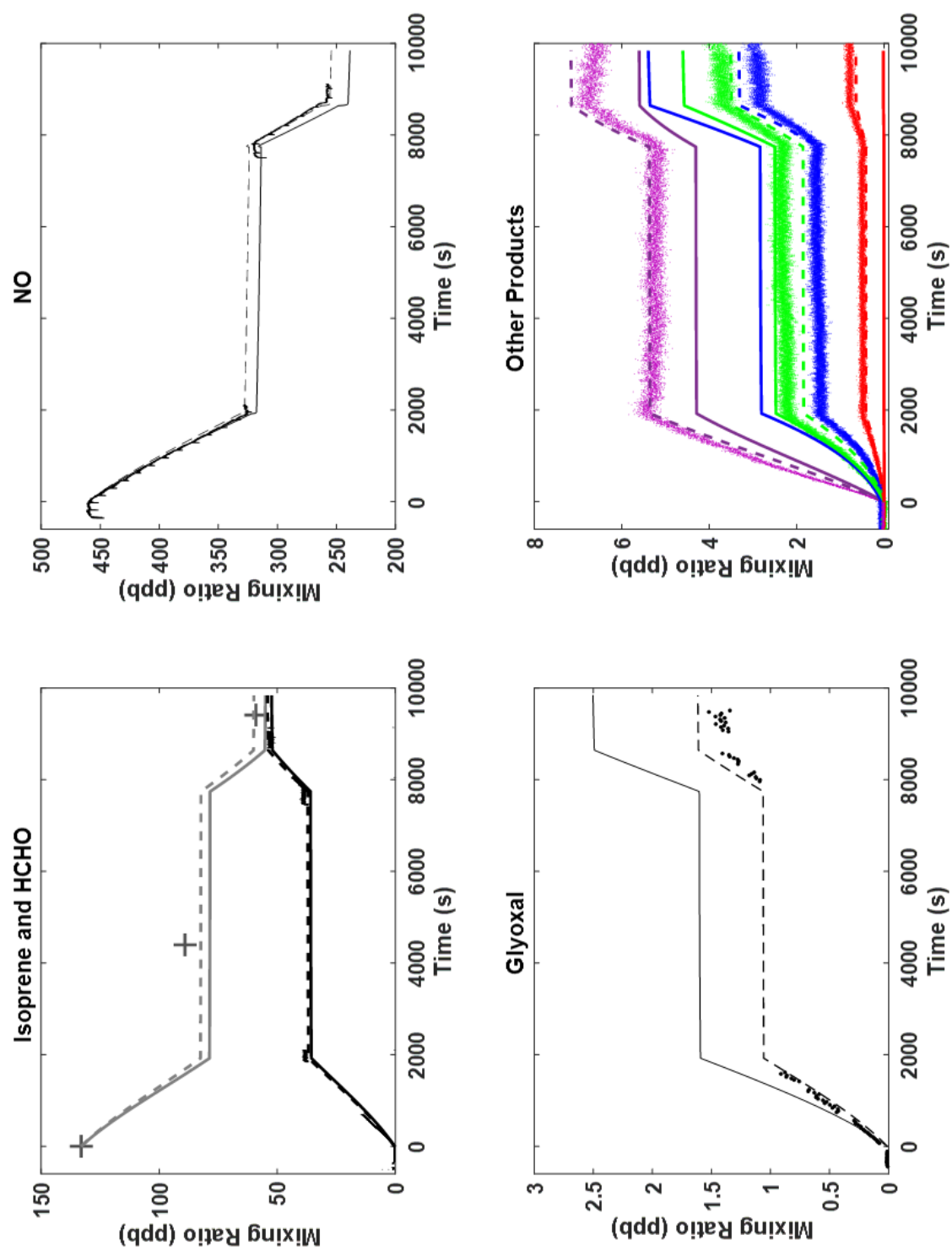


Figure 3.12: Isoprene High NO_x oxidation. Compounds plotted are isoprene (grey), HCHO (black), isoprene nitrates (purple), C4Diols (red), hydroxyacetone (green) and glycolaldehyde (blue) along with glyoxal and NO. Solid line = MCM Dashed line = This Work

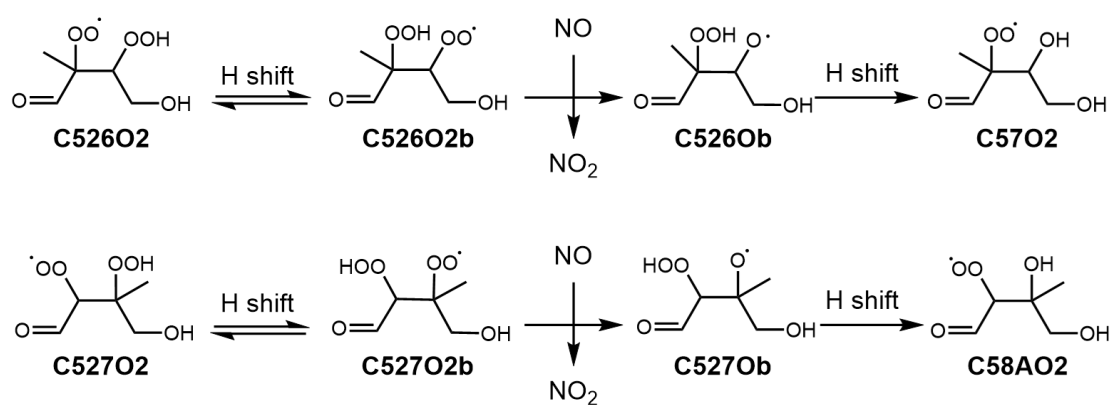


Figure 3.13: Changes to the C526O2 and C527O2 decomposition pathways. These changes enable the formation of C4 diol directly from isoprene under High NO_x conditions. A hydrogen shift followed by reaction with NO and another hydrogen shift is required to form the alcohol group. This process leads to the same RO₂ species that form from IEPOX oxidation so their chemistry has been described previously in this work.

3.4.2 LOW- NO_X EXPERIMENTS

Using H_2O_2 as the OH source during low NO_X oxidation conditions leads to relatively high levels of HO_2 . However, the self-reaction of HO_2 limits the amount of this radical that can be present in the system. This leads to a larger RO_2 bimolecular reaction lifetime than experiments under high NO_X conditions, providing additional time for unimolecular or isomerization reactions. In our low NO_X experiments the concentration of HO_2 was about 70 ppt, leading to a peroxy radical lifetime of 14 s which is larger than the one in the slow-chem experiments (next section). For allylic radicals like the main isoprene peroxy radicals, it means that the RO_2 population has time to establish a thermodynamic distribution. This is relevant for the isoprene experiment and the ISOPOOH experiments to a smaller extent.

Under low NO_X conditions RO_2 radicals can react with HO_2 to form organic peroxides. The reaction of HO_2 and RO_2 has also been shown to recycle OH, yielding an alkoxy radical in the process. This can be via direct formation of OH, O_2 and RO or by decomposition of the peroxide immediately upon formation. OH recycling has been shown to be enhanced in highly functionalized carbon skeletons, in part due to hydrogen bonding.⁴⁵

OH regeneration with alkoxy radical formation can explain the products we observed during these experiments but only to a certain extent. The chemistry of IEPOX and ISOPOOH must have the same initial RO_2 branching ratios that we used during the high NO_X experiment. The alkoxy radicals formed in these conditions are the same as those formed under high NO_X conditions and their decomposition has been characterized. Using only the reactions of HO_2 and RO_2 the C4 diol and HCHO levels observed during the IEPOX experiments cannot be accounted for without overestimating other products. For these reasons, the low NO_X experiments require a mixture of hydroperoxide formation, OH regeneration and RO_2 isomerization reactions to explain the observed products and their yields.

IEPOX

Oxidation of IEPOX under low NO_X conditions has two main products: C4 diols and formaldehyde. The MCM features isomerization reactions for C57O2 and C58AO2 that yield CO and C4 diols and OH. In these reactions the peroxy radical abstracts a hydrogen from an aldehyde group in an adjacent carbon. These reactions use the “K14ISOM1” rate. This rate is very fast (0.57 s^{-1} at 298 K) accounting for >90% of the fate of these RO_2 under our experimental conditions. This leads to an overestimation of C4 diols in the MCM by a factor of 3. It also leads to an underestimation of every other product we observed. Lowering these isomerization reaction rates fixes the overestimation of C4 diols but cannot explain the rest of the products.

The main source of HCHO from IEPOX is the C59O2 branch of products. This branch does not feature an isomerization reaction in the MCM. This is in contrast to the observed amounts of HCHO and comparatively low hydroxyacetone found in the cis-IEPOX experiment. An isomerization reaction is required in order to match the HCHO and hydroxyacetone values observed during the oxidation of cis-IEPOX. This reaction would lead to OH, HCHO and BIACETOH. The alkoxy radical pathway alone can explain the observed formaldehyde but would lead to a large overprediction of hydroxyacetone. The amount HCHO observed during these experiments requires all of the C59O2 formed to lead to HCHO. This implies no peroxide formation from this RO_2 branch. Such a reaction is not needed in the case of trans-IEPOX, where assuming a 100% yield of C59O from $\text{RO}_2 + \text{HO}_2$ captures the HCHO to hydroxyacetone ratio perfectly.

The only way 3 and 2 carbon products can compete with isomerization reactions under these conditions is if they also are products of isomerization reactions to some extent. We added a 1,5 isomerization reaction that leads to 3 and 2 carbon products to account for the observed levels of hydroxyacetone, glycolaldehyde and glyoxal. It is important to note that we are unable to determine the actual rate at which these isomerization reactions occur with these experiments. These are likely

not the rates at which these reactions occur if they occur at all. We recommend that the K14ISOM1 reaction is scaled according to the values shown in table 3.5 as these values match the observations made during our experiments. Additional work must be performed to study the fate of highly functionalized peroxy radicals under timescales relevant to atmospheric conditions. The model results of the IEPOX low NO_x experiments and the changes made in this work are shown in figure 3.14 and figure 3.15.

IEPOX Low NO_x Model Changes				
Peroxy Radical	1,4 Scaling	1,5 Scaling	RO + OH	ROOH
cC57O2	0.17	0.03	0%	100%
cC58AO2	0.15	0.05	0%	100%
cC59O2	-	0.12	100%	0%
tC57O2	0.17	0.03	0%	100%
tC58AO2	0.17	0.02	0%	100%
tC59O2	-	-	100%	0%

Table 3.5: Suggested reaction rates for isomerization reactions and branching of the $\text{RO}_2 + \text{HO}_2$ reaction. Formation of peroxides was allowed except for the C59O2 peroxy radical. This radical led almost exclusively to HCHO in both instances.

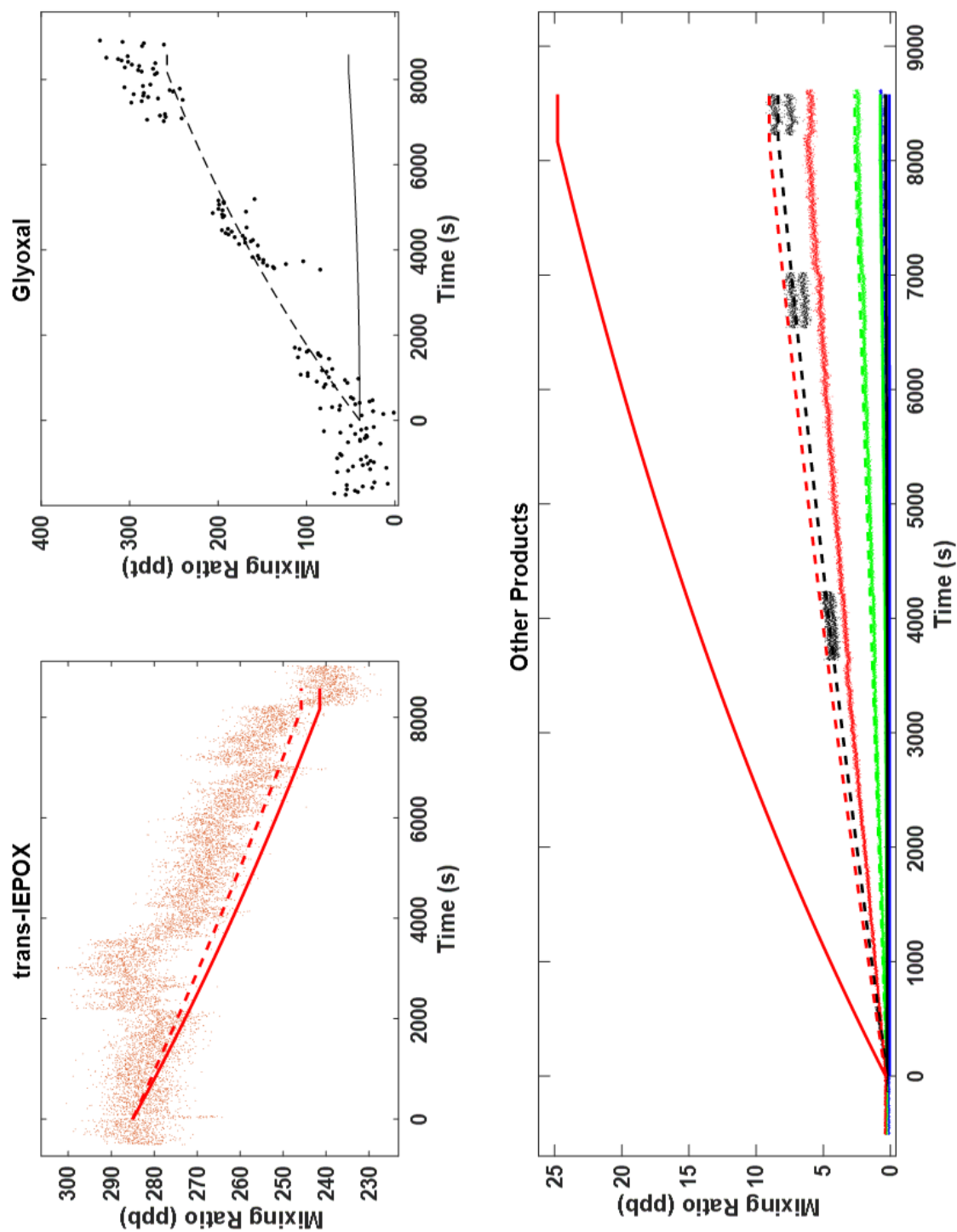


Figure 3.14: trans-IEPOX Low NO_x Oxidation. Products observed are glyoxal, formaldehyde (black), C4Diols (red), hydroxyacetone (green) and glycolaldehyde (blue). Solid line = MCM Dashed line = This Work

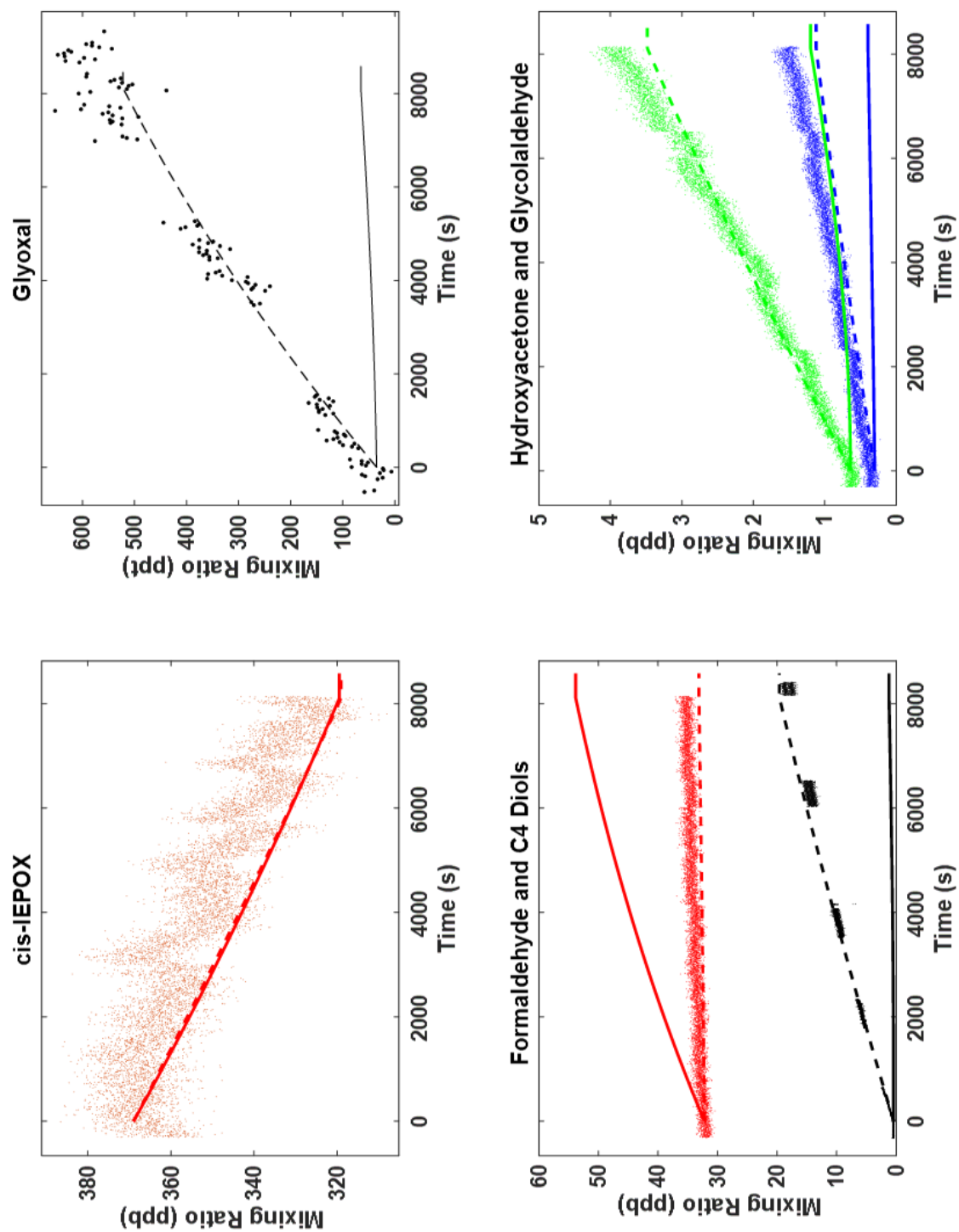


Figure 3.15: cis-IEPOX Low NO_x Oxidation. Products observed are glyoxal, formaldehyde (black), C4Diols (red), hydroxyacetone (green) and glycolaldehyde (blue). Solid line = MCM Dashed line = This Work

ISOPOOH

ISOPOOH oxidation under low NO_X conditions is expected to have a higher IEPOX yield. This is due to the peroxide hydrogen abstraction pathway leading to the regeneration of ISOPOOH. This pathway can also lead to HPALD formation due to O_2 loss and readdition. Additionally, the products of the OH and O_2 addition pathway (ISOPB(D)OOHO₂) can lead to isoprene dihydroxy dihydroperoxide after reaction with HO_2 we call this species (ISOPB(D)OOHOOH). If this reaction instead recycles OH, the formed alkoxy radical is expected to abstract a hydrogen from the neighboring hydroperoxide group, leading to ISOPB(D)OOHOHO₂. The same process can happen with this species leading to a hydroperoxide triol which we termed ISOPB(D)OOHOHOOH or fragmentation products via the OH recycling pathway. We cannot measure these peroxides with the instruments used in this study. We assume that the main loss pathway of these highly functionalized hydroperoxides is to the chamber walls and that the initial branching of ISOPB(D)OOHO₂ + HO_2 to yield ISOPB(D)OOHOOH is the total expected RO_2 + HO_2 yield of hydroperoxides in the absence of isomerization reactions.

Another feature of the low NO_X ISOPOOH oxidation pathway is large yields of C₄ diols relative to hydroxyacetone and glycolaldehyde. In a manner similar to IEPOX, these yields cannot be explained solely by the reaction between the relevant RO_2 + HO_2 leading to RO + OH. The relative amounts of C₄ diols are much larger than under high NO_X conditions which suggests that alkoxy radicals are not their source. We suggest that isomerization reactions are taking place in this system as well. The low NO_X OH+ O_2 addition pathways for 1,2-ISOPOOH and 4,3-ISOPOOH are shown in figures 3.16 and 3.17. In order to make the model match we included isomerization reactions that fill the gap in products that OH regeneration and alkoxy radical decomposition cannot. Results are shown in figures 3.18 and 3.19.

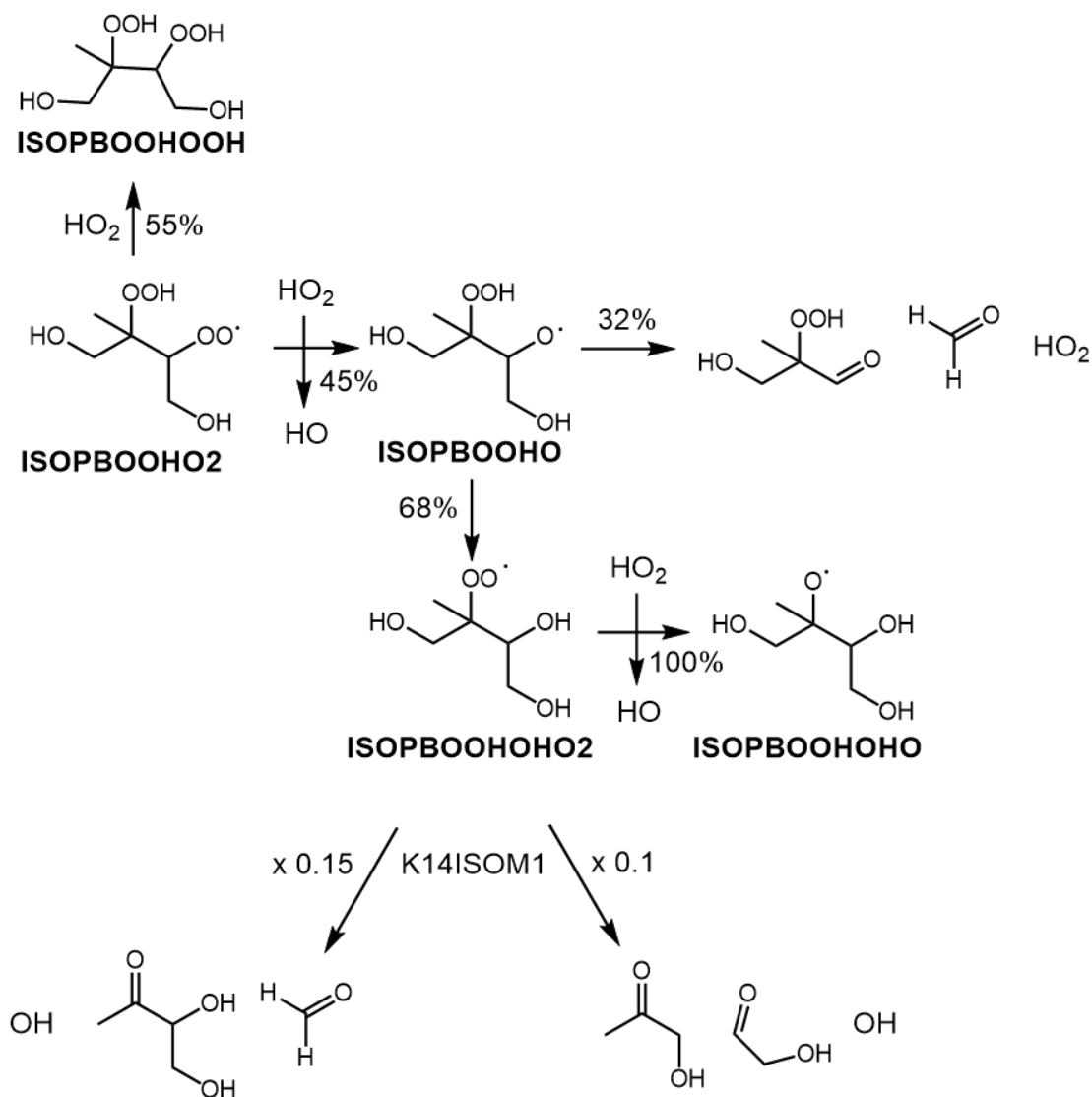


Figure 3.16: Oxidation scheme for the low NO_x oxidation of 1,2-ISOPPOOH. Formation of hydroperoxides can occur at both ISOPBOOHOOH2 and ISOPBOOHOOH. However, since these hydroperoxides were not measured we assumed their formation in the first step (55%). 45% of the ISOPBOOHOOH2 branching ratio can account for the observed products. Isomerization reactions have OH as a co-product. Decomposition reactions have HO_2 as a co-product.

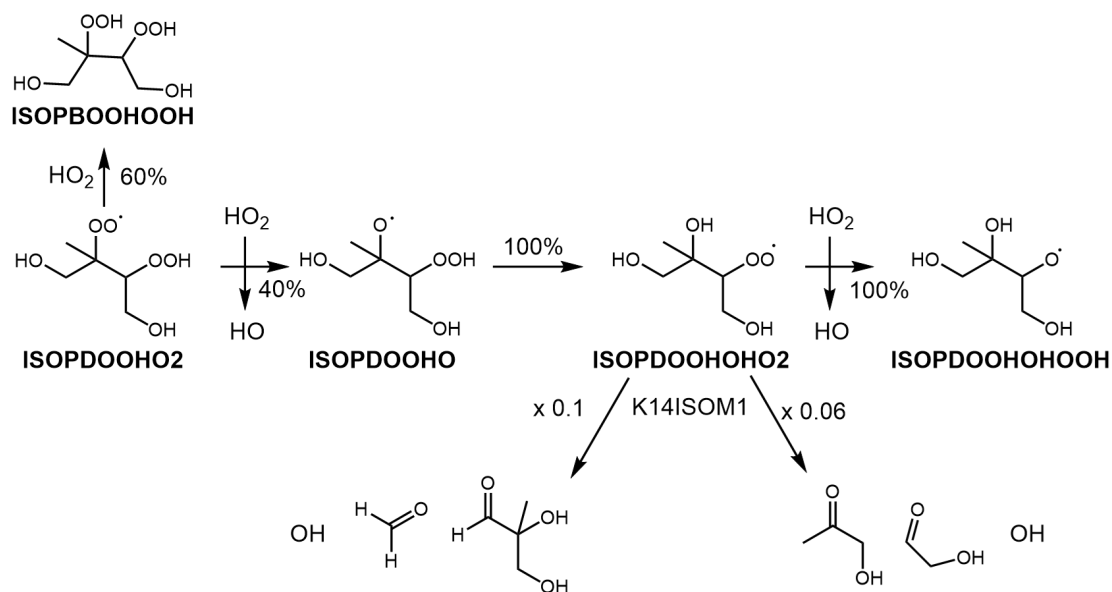


Figure 3.17: Oxidation scheme for the low NO_x oxidation of 4,3-ISOPDOOH. No C4 hydroperoxide is formed in this pathway since HCHO is overpredicted for this experiment while slightly underpredicting C4 diols.

Recently, ISOPB(D)OOHO₂ has been proposed to isomerize by abstracting a hydrogen from a neighboring carbon, leading to an epoxide intermediate.²³ This isomerization can be included in these experiments at the expense of the ISOPB(D)OOHOOH yield. If we assume that only OH regeneration or isomerization occurs, the isomerization rate cannot be faster than 0.06 s⁻¹ for 1,2-ISOPOOH and 0.1 s⁻¹ for 4,3-ISOPOOH, a faster rate leads to an underprediction of other O₂ addition products. Including this rate lowers the ISOPB(D)OOHOOH yield dramatically, even though it's been shown to contribute significantly to SOA in previous experiments.

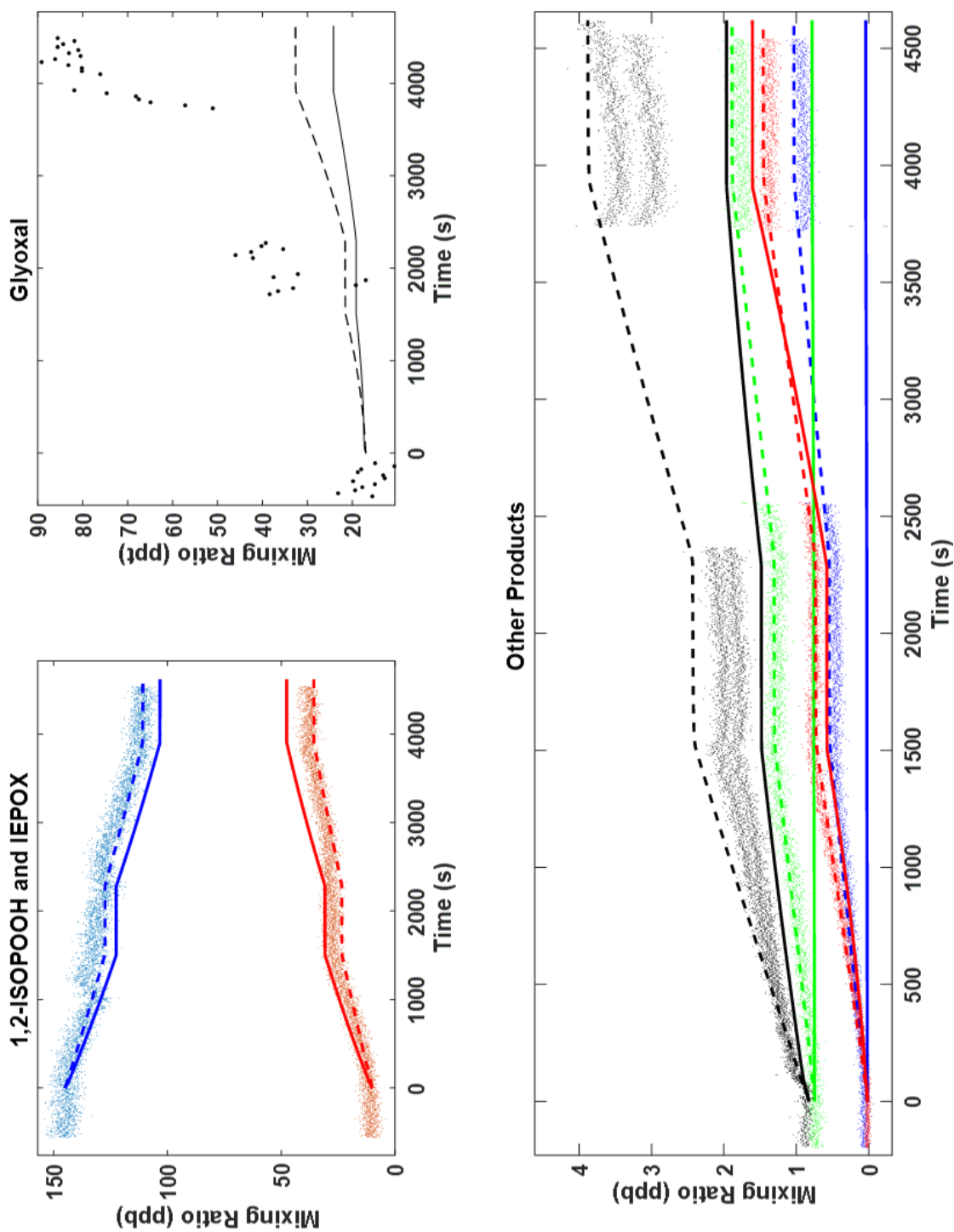


Figure 3.18: 1,2-ISOPOOH Low NO_x oxidation. Species plotted are 1,2-ISOPOOH (light blue), IEPOX (orange), C4Diol (red), hydroxyacetone (green), glycolaldehyde (blue), HCHO (black) and glyoxal. Solid line = MCM Dashed line = This Work

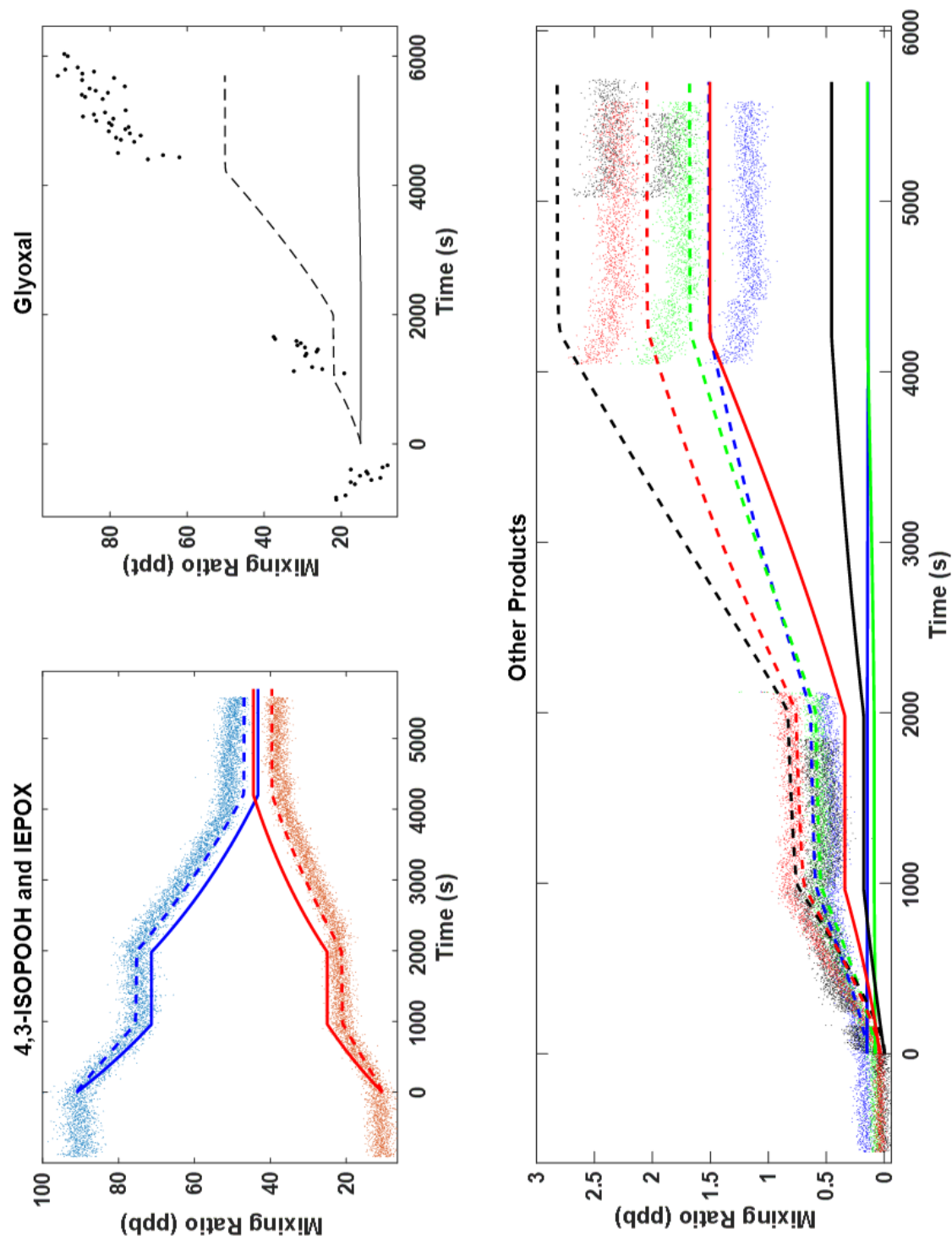


Figure 3.19: 4,3-ISOPOOH Low NO_x oxidation. Species plotted are 4,3-ISOPOOH (light blue), IEPOX (orange), C4Diol (red), hydroxyacetone (green), glycolaldehyde (blue), HCHO (black) and glyoxal. Solid line = MCM Dashed line = This Work

ISOPRENE

Under low NO_x conditions, isoprene oxidation generates ISOPOOH and IEPOX isomers which were discussed in the previous sections. These products are overestimated by the MCM as shown in figure 3.20. This overestimation is due to an underrepresentation of RO_2 - RO_2 chemistry. The main RO_2 species in this experiment is the ISOPBO2 radical. This radical reaches concentrations of 200 ppt (modeled) during our experiment. The RO_2 - RO_2 chemistry of isoprene RO_2 s was studied in detail by Jenkin et al.⁵⁰ The reported RO_2 - RO_2 reaction rates are on the order of 2.5×10^{-12} with the exception of tertiary RO_2 self reactions which are two orders of magnitude slower. The second highest RO_2 radical by abundance is the ISOPDO2 peroxy radical (80 ppt, modeled). The reaction of ISOPBO2 and ISOPDO2 is about a factor of 4 faster than the current RO_2 - RO_2 reaction rate for ISOPBO2. Increasing this reaction rate lowers the ISOPOOH yield dramatically. Furthermore, in order for this reaction to account for the observed formaldehyde yield, the products of these reactions should be ISOPBOH, an isoprene diol, and HCOC5, a carbonyl product discussed in the oxidation of ISOPDOOH. These are the products predicted by the Russell mechanism. With these facts in mind, we increased the RO_2 - RO_2 reaction rate for ISOPBO2 and the distribution of its products to form primarily ISOPBOH and in the case of ISOPDO2, HCOC5. This branching ratio goes against the expected value for these products, which are about 10%. It is unclear whether this difference arises from differences in RO_2 radical populations in flash photolysis experiments and typical environmental chamber conditions. These changes to RO_2 - RO_2 chemistry are required to explain the results of this chamber experiment but are not necessarily needed to explain ambient measurements.

The oxidation of ISOPBOH is not likely to occur as represented in the MCM. OH addition to the double bond should lead to the ISOPBOOH₂ peroxyradical that was described in the ISOPOOH oxidation section. Assuming a 100% yield of ISOPBOOH₂ from ISOPBOH

leads to a large over prediction of C4 diols, hydroxyacetone and glycolaldehyde. This overprediction could be due to an isomerization reaction of ISOPBOOH₂ that is not included in this work. The main formation channel for C4 diols under low NO_x conditions are the reactions added for ISOPOOH and a contribution from ISOPBOH. They capture C4 diol production without needing any additional changes since they were optimized under low NO_x conditions in the previous sections.

There is significant speculation in the modelling community regarding glyoxal production from isoprene oxidation under low NO_x conditions.⁶⁵ In the MCM, under low NO_x, glyoxal production occurs mainly through the formation of the C537O alkoxy radical and its decomposition. The MCM severely underpredicts the amount of glyoxal expected under these conditions while over predicting it under high NO_x conditions. This was remediated by adjusting the yield of C537OOH by changing the C537O₂ and HO₂ reaction to yield C537O and OH 50% of the time.

Formation of glycolaldehyde is difficult to match in our experiments. The MCM underpredicts this product and while our changes to ISOPOOH and IEPOX make the agreement better, the main source of this product continues to be oxidation of MVK and ISOPBOH. The updated version of the model contains changes to the chemistry of MVK as recommended by Praske et al.⁸³ The amount of glycolaldehyde that can come from ISOPBOH is limited by the C4 diols, which are properly represented in this version of the model. As for MVK/MACR, their yield is limited by the isomerization reactions of the δ peroxy radicals, RO₂-RO₂ reactions and the efficiency of ISOPOOH formation. Since HCHO is well matched by the model, additional formation of MVK seems unlikely. The next major source of glycolaldehyde is HPALD photolysis. Part of the changes implemented from Teng et al.¹⁰¹ were changes to HPALD yields (adjusted to 25%) from all branches that make it, in agreement with recently published data. HPALD photolysis has two pathways which were adjusted to only the one that yields glycolaldehyde, acetyl peroxy radical and OH. Further experiments with HPALD standards are required to understand its photolysis and photooxidation as

it is vital to understand isoprene oxidation in remote environments.

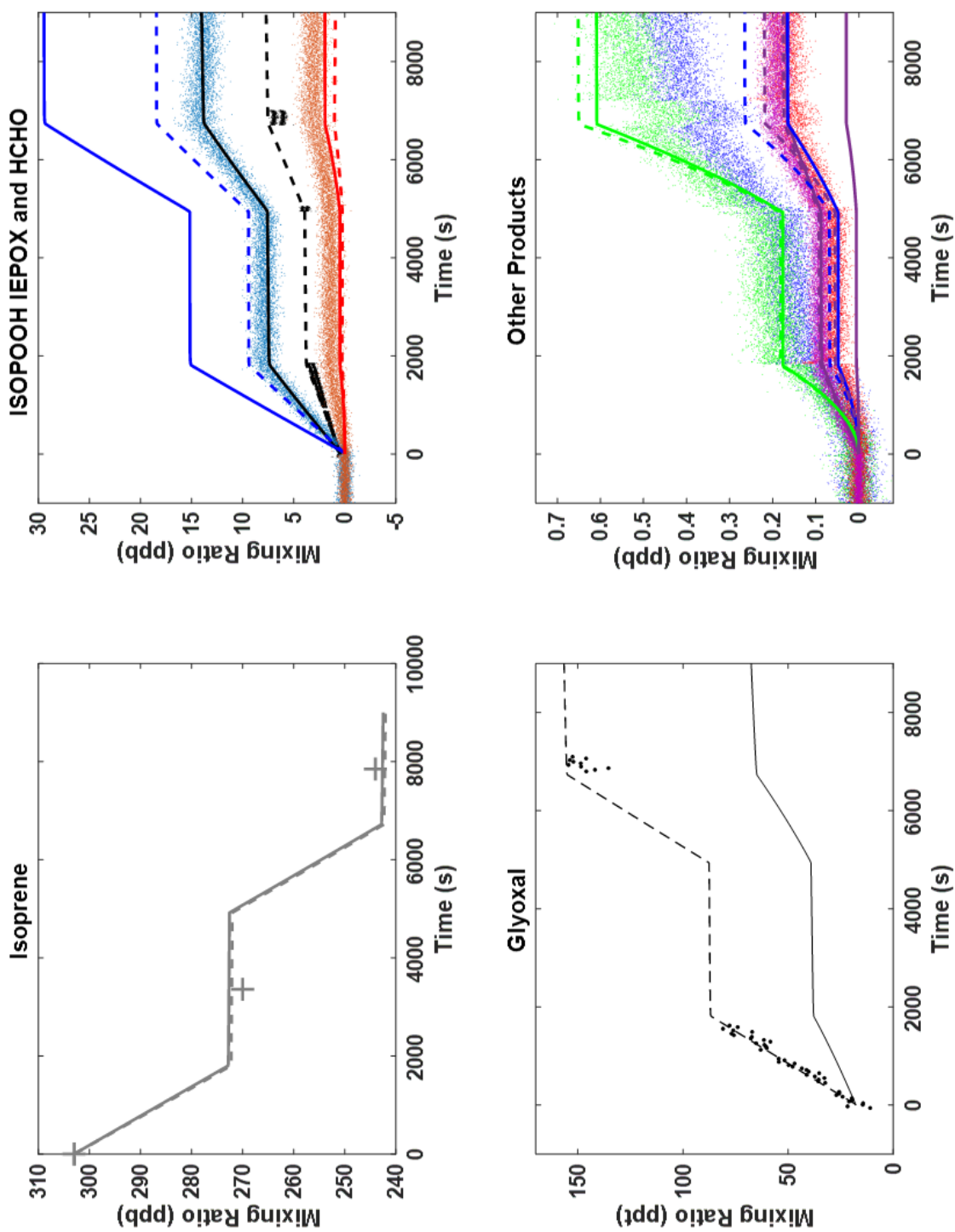


Figure 3.20: Isoprene Low NO_x oxidation. Compounds plotted are isoprene, ISOPOOH (light blue), HCHO (black), IEPOX (orange), glyoxal, hydroxyacetone (green), glycolaldehyde (blue), isoprene nitrates (purple) and C4Diols (red). Solid line = MCM Dashed line = This Work

3.4.3 SLOW-CHEM EXPERIMENTS

IEPOX

A slow-chem experiment was performed with trans-IEPOX and it is shown in figure 3.21. The IEPOX trace is relatively unstable and appears to suffer from wall losses in the second part of the experiment as the volume of the environmental chamber is depleted. NO_x is relatively well captured by both models. The MCM overpredicts glyoxal, and C4 diols under these conditions while underpredicting formaldehyde and glycolaldehyde. Isomerization reactions were already required for the model to reproduce the low NO_x experiments since $\text{HO}_2 + \text{RO}_2$ reactions did not adequately match the observed product ratios. However, the peroxy radical lifetime in low NO_x experiments was longer than under slow-chem conditions (14 and 16 s respectively). The isomerization rates had to be increased to match the observed yields of glyoxal and glycolaldehyde in this experiment which were quite low. This lead to a slight over prediction of C4 Diol production but a good match in every other product except for hydroxyacetone, whose concentration was not matched in our model but well predicted by the MCM.

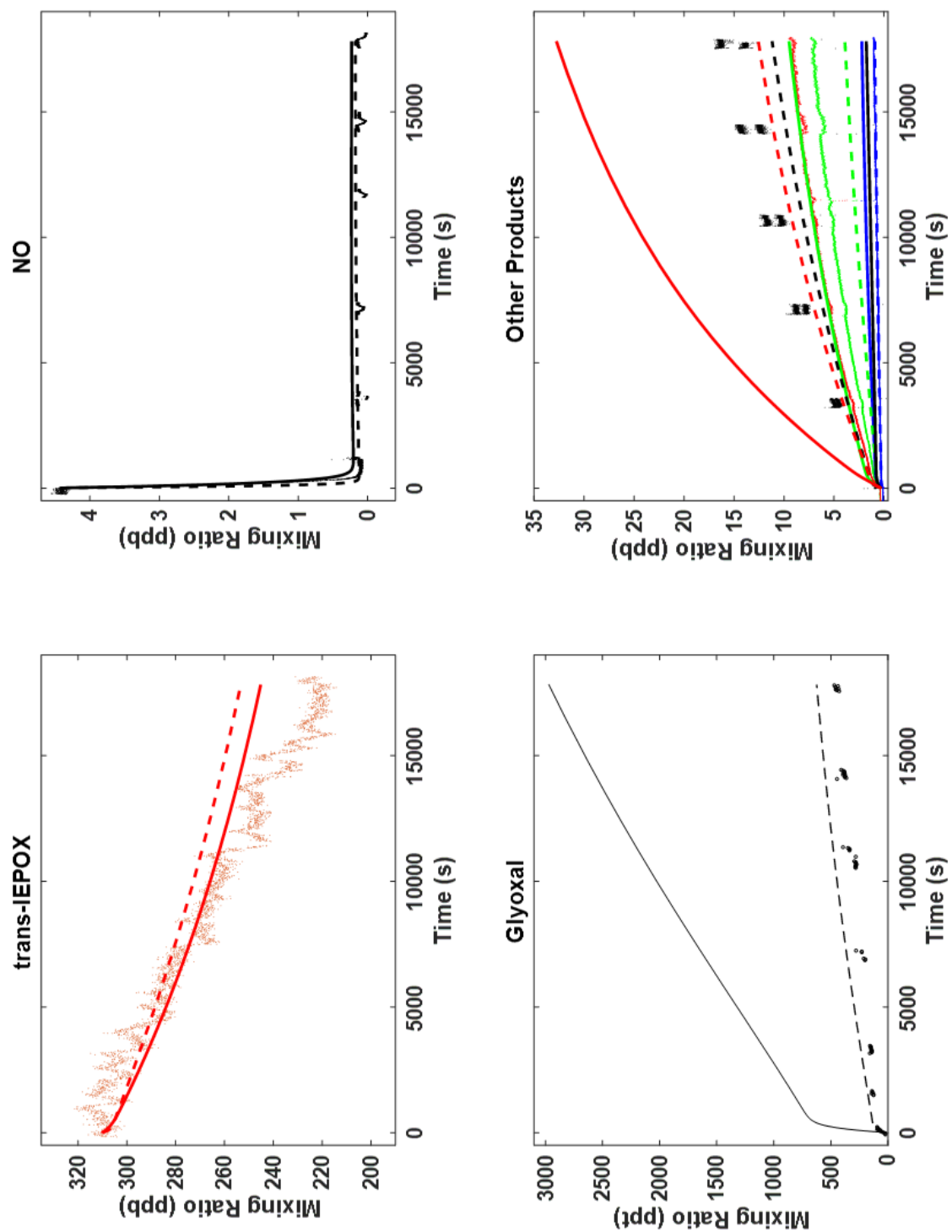


Figure 3.21: trans-IEPOX Slow-Chem oxidation. Compounds plotted are IEPOX, NO, glyoxal, HCHO (black), hydroxyacetone (green), glycolaldehyde (blue) and C4Diols (red). Solid line = MCM Dashed line = This Work

ISOPOOH

The oxidation of 1,2-ISOPOOH under slow-chem conditions is shown in figure 3.22. These experiments did not require any further changes to match the observed products. Increasing the temperature by 25 degrees does not cause significant changes to the products or model performance (Figure 3.23). This is because isomerization reactions are already fast enough at room temperature to compete with the reactions with NO and HO₂. Additionally, the introduction of isomerization reactions was needed for the low NO_x experiments since the product ratios suggest that their production is not from alkoxy radical chemistry, which was already described under high NO_x conditions.

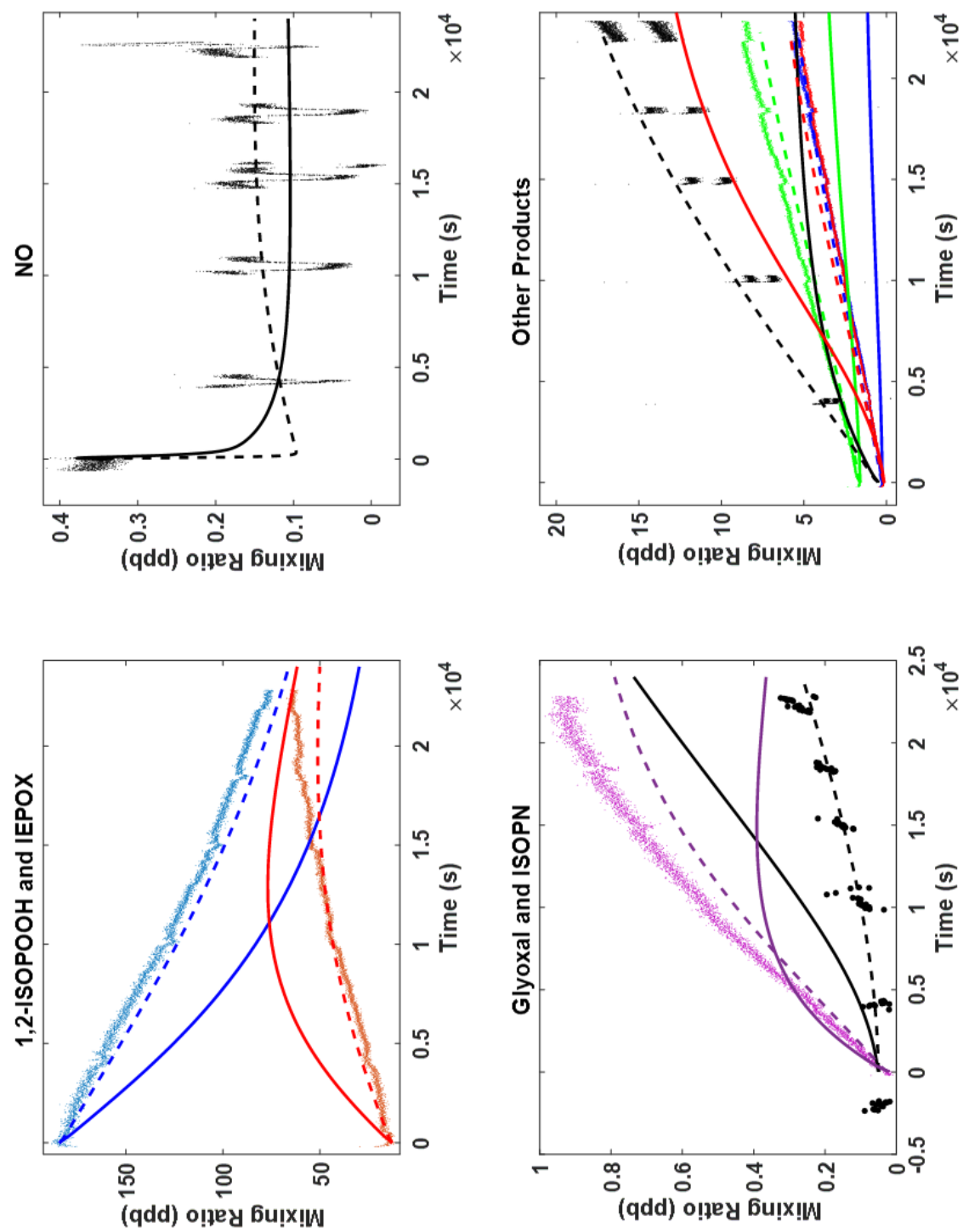


Figure 3.22: 1,2-ISOPOOH Slow-Chem oxidation. Species plotted are 1,2-ISOPOOH (light blue), IEPOX (orange), NO, isoprene nitrates (purple), glyoxal (black), C4Diol (red), hydroxyacetone (green), glycolaldehyde (blue), HCHO (black). Solid line = MCM Dashed line = This Work

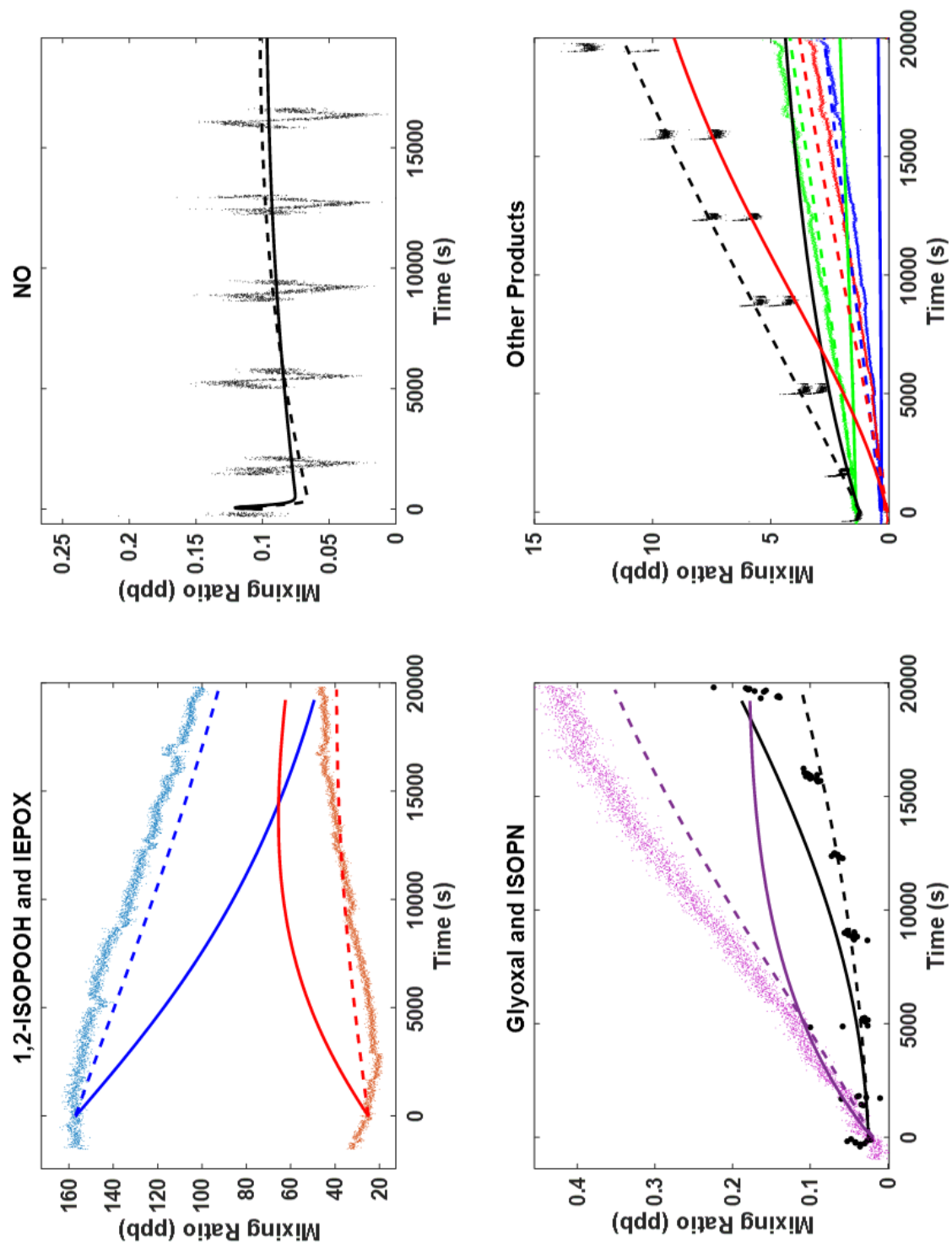


Figure 3.23: 1,2-ISOPOOH Slow-Chem high temperature oxidation. Species plotted are 1,2-ISOPOOH (light blue), IEPOX (orange), NO, isoprene nitrates (purple), glyoxal (black), C4Diol (red), hydroxyacetone (green), glycolaldehyde (blue), HCHO (black). Solid line = MCM Dashed line = This Work

ISOPRENE

We performed two isoprene slow-chem experiments to investigate the effects of temperature on the observed products (Figures 3.24 and 3.25). We will discuss the room temperature experiment first. The MCM and the update model show a similar amount of oxidation for isoprene. Unfortunately, the byproduct of isopropyl nitrite photolysis, acetone, has a similar retention time as isoprene in our GC-FID measurements. We corrected for this interference but we suspect that the GC measurement might be an overestimate of the isoprene concentration.

Formaldehyde, ISOPOOH and IEPOX are slightly underpredicted but within experimental uncertainty. The formation of glyoxal is well captured by the MCM although slightly underpredicted. All other products are underpredicted towards the second part of the experiment. The model does a particularly bad job at predicting the yields of hydroxyacetone and glycolaldehyde, a fact that does not improve with the changes made in our version of the model. Isoprene nitrates are also underpredicted by the MCM which is expected since their yield has not been updated as it was for our version of the model. The changes made to our model to fit the low and high NO_x isoprene experiments do not make a large difference in these experiments.

The high temperature experiment was performed at 318 K. Both versions of the model over oxidize isoprene. The same interference by acetone might be the reason why we see this difference. Formaldehyde and glyoxal are predicted by the model reasonably well under both our version of the model and the MCM. Isoprene nitrates are significantly overpredicted under these experimental conditions by both versions of the model. This overprediction is the result of either a hindered nitrate yield at high temperatures or the presence of O_3 in the chamber. A model run including around 15 ppb of O_3 improves the model performance for isoprene nitrates and glyoxal. The missing glycolaldehyde, hydroxy acetone and C_4 diols cannot be explained with this mechanism. Additional experiments must be performed to understand the source of these products from isoprene

oxidation under slow-chem conditions.

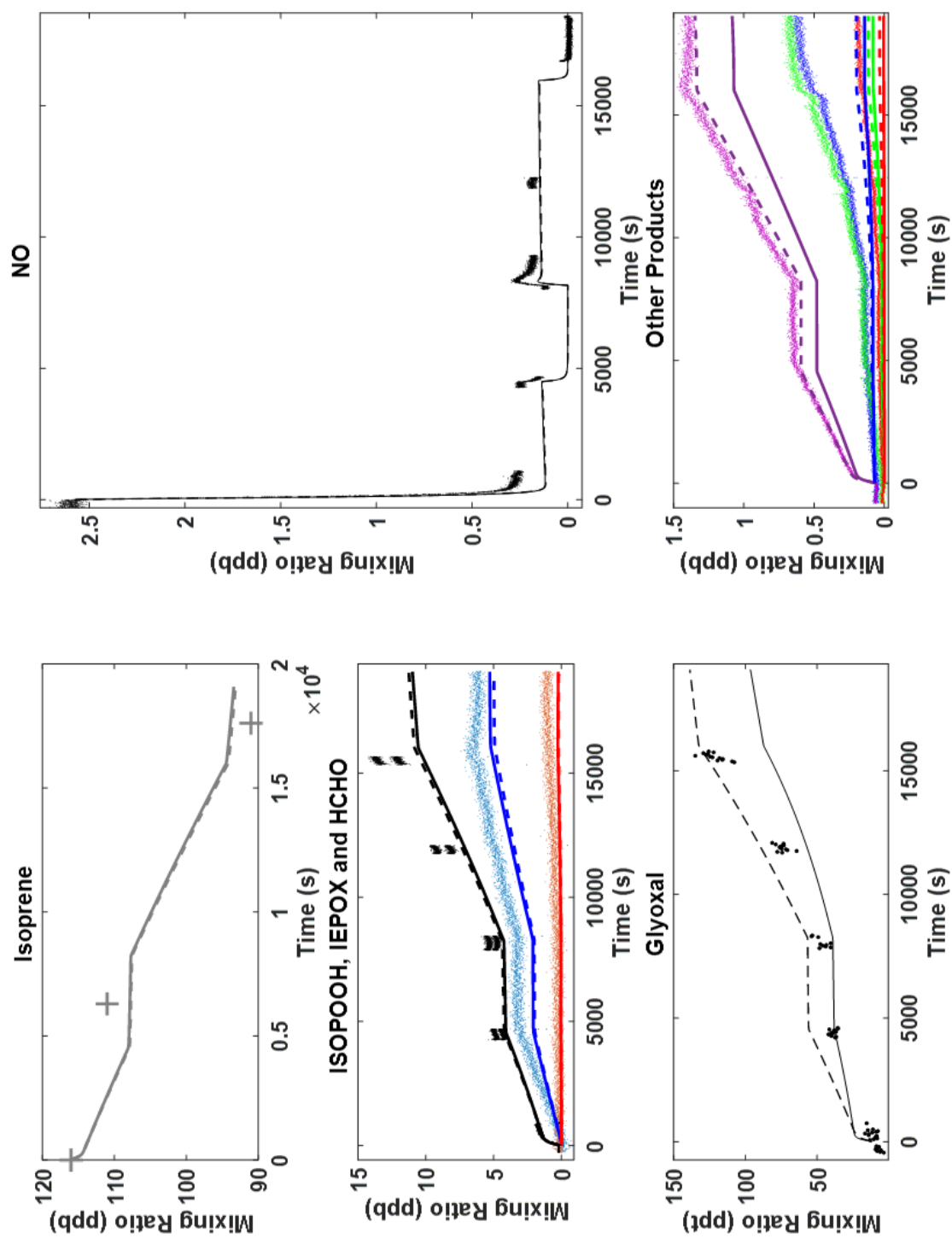


Figure 3.24: Isoprene Slow-Chem oxidation. Species plotted are isoprene, NO, HCHO (black), ISOPOOH (light blue), IEPOX (orange), glyoxal, isoprene nitrates (purple), C4Diol (red), hydroxyacetone (green), glycolaldehyde (blue). Solid line = MCM Dashed line = This Work

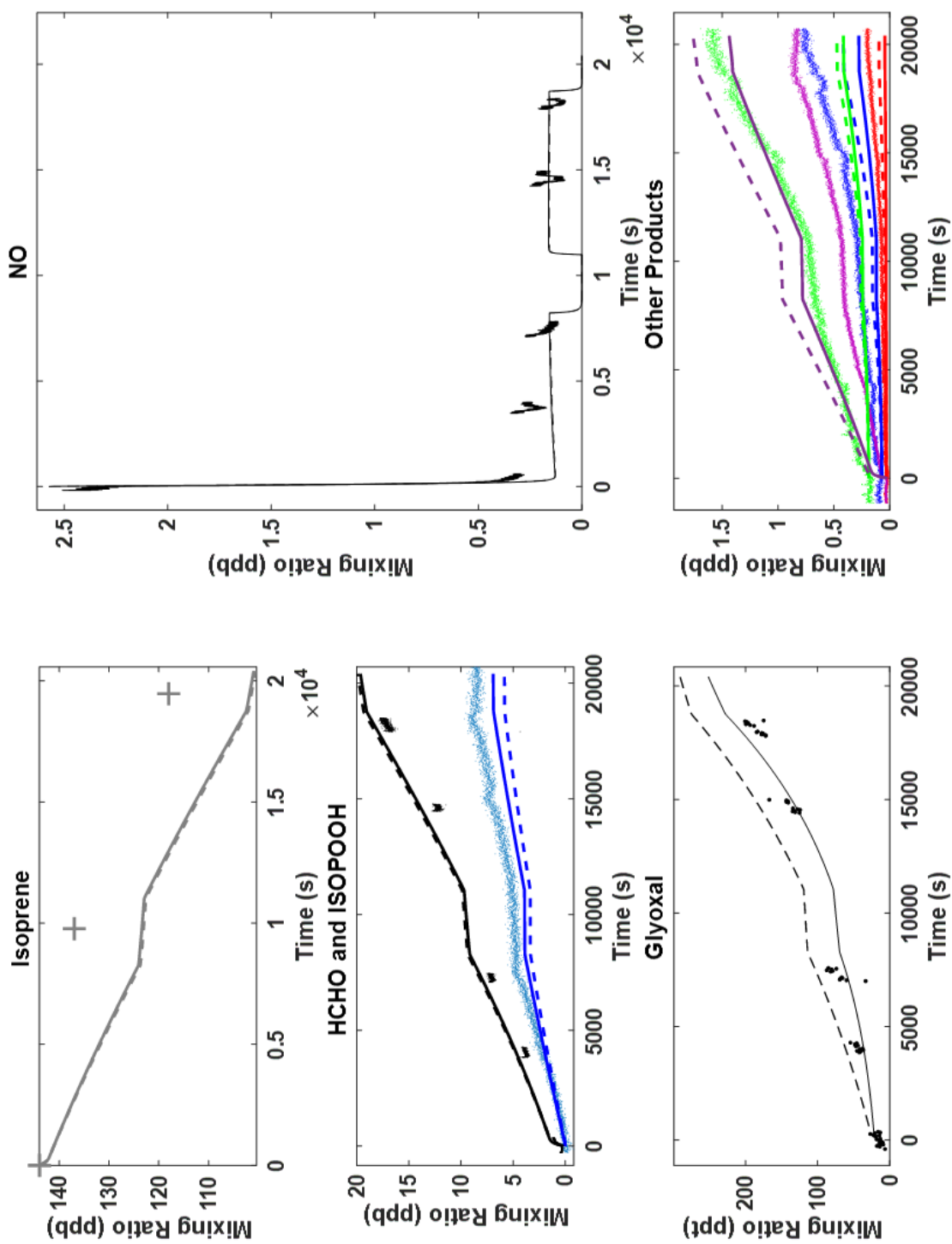


Figure 3.25: Isoprene Slow-Chem High Temperature. Species plotted are isoprene, NO, HCHO (black), ISOPOOH (light blue), glyoxal, isoprene nitrates (purple), C4Diol (red), hydroxyacetone (green), glycolaldehyde (blue). Solid line = MCM Dashed line = This Work

3.4.4 GEOS-CHEM MODEL RESULTS

GEOS-Chem is a global three-dimensional model of atmospheric chemistry.⁶ It has been developed for decades by the atmospheric chemistry modeling group at Harvard University. The chemistry of isoprene is vital to the performance of this model. The model continues to be updated as new developments in the oxidation of isoprene emerge, allowing us to examine the effects of these changes on a global scale. Unfortunately, it is not computationally feasible for a global model to include as many species and reactions as the MCM.

For this study, the total glyoxal production from isoprene oxidation in GEOS-Chem was matched with the values observed in our experiments. In addition, the changes to ISOPOOH and IEPOX chemistry were implemented within the heavily parametrized oxidation scheme in GEOS-Chem. Additional changes had to be made in order for the models to agree. These changes included: 1) increasing the glyoxal yield from glycolaldehyde to match that of the MCM, 2) an increase of the glycolaldehyde + OH reaction rate to match the MCM, 3) an increase in the glycolaldehyde yield from MVK oxidation under high- NO_x conditions, 4) removal of the glyoxal yield from HPALD oxidation by OH, 5) an increase in the glycolaldehyde yield from isoprene nitrate oxidation, 6) changes to C4 hydroxy dicarbonyls to yield methylglyoxal instead of glycolaldehyde and most importantly 7) changing the MCK/MACR distribution to match ambient values.

The results of these changes are shown in figures 3.26-27. HCHO concentrations increased as much as 15% on a global scale. This change is concentrated in the tropics where isoprene emissions dominate the chemistry. Enhancements of around 5% are also observed in the SE US. The opposite trend is observed for glyoxal. The concentration of glyoxal in the tropics was reduced by around 10%. The base GEOS-Chem model seems to have overpredicted glyoxal concentrations under low- NO_x conditions while underpredicting them under high- NO_x conditions, this is shown by an increase in glyoxal over NE US, Europe and China.

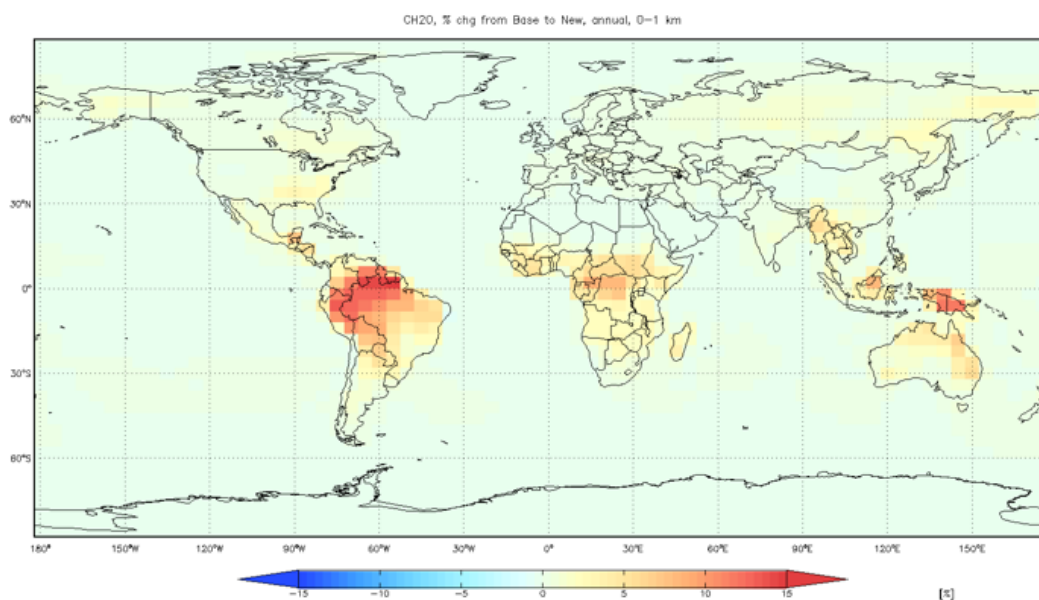


Figure 3.26: GEOS-Chem was updated to include the changes we made to ISOPOOH and IEPOX chemistry. Formaldehyde is increased over the tropics which are low- NO_x oxidation environments and where most isoprene emissions take place.

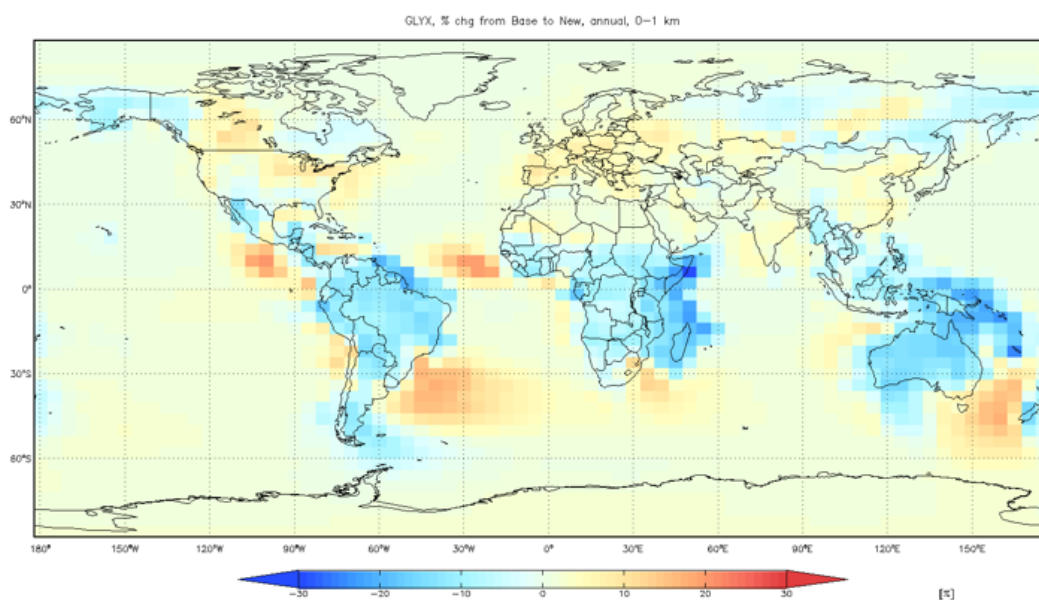


Figure 3.27: GEOS-Chem was updated to include the changes we made to ISOPOOH and IEPOX chemistry. Glyoxal is reduced over the tropics where low- NO_x oxidation of isoprene takes place. However, there is a slight increase in glyoxal in regions with high- NO_x concentrations.

3.5 CONCLUSIONS

We performed a series of chamber experiments to understand the oxidation of isoprene low NO_X products under a variety of conditions. For IEPOX, the mechanism currently implemented in the MCM is sufficient to explain our observations after changes to the observed yields and isomerization rates. Importantly, the chemistry of the cis and trans isomers of IEPOX must be separated for the model to represent these species accurately. Isomerization reactions are not only expected but required for the model to represent the observed products. A large yield of formaldehyde is observed in the IEPOX experiments, a yield that is consistent with experiments beginning with ISOPPOOH. The yield of formaldehyde is often larger than the yield of hydroxyacetone, which is only possible if the formaldehyde is produced from reaction of IEPOX at the epoxide hydrogen. Unfortunately, large background production reduces the accuracy of the formaldehyde yield though the results showcased in this model are a reasonable representation. This yield could be increased if the concentration of IEPOX is overestimated in these experiments. The MCM significantly overpredicts the yields of C4 Diols under low NO_X conditions. This overestimate was redistributed to other products in order to match our observations. The same process took place with the overestimation of glycolaldehyde and hydroxyacetone under high NO_X conditions. Nevertheless, isomerization reactions should be considered the main reaction pathway for the initial IEPOX RO_2 radicals under typical atmospheric conditions.

ISOPPOOH oxidation in the MCM does not feature an O_2 addition pathway. This pathway is necessary to account for the direct yield of C4 diols, glycolaldehyde and hydroxyacetone. OH regeneration accounts for 40-45% of the reactions of the O_2 addition pathway under low NO_X conditions. The remaining 55-60% either undergoes isomerization or forms dihydroxy dihydroperoxides which are lost to the chamber walls. Our experiments suggest that applying the isomerization rate of methacrolein to other species with the same functional group motif may not be appropriate, lead-

ing to isomerization rates that are too fast. For highly functionalized RO₂s, the reaction with HO₂ might have a lower yield of peroxides than previously assumed, which in addition to isomerization reactions, can lead to sustained OH levels in remote regions.

Changes to isoprene chemistry fine tuned the yield of glyoxal under high and low NO_x conditions. Under high NO_x conditions the glyoxal yield was reduced by redirecting some of the C₅H₇O₂ and C₅H₆O₂ radicals towards the formation of C₄ diols instead of glyoxal, matching the observed concentrations of both species. Under low NO_x, agreement with glyoxal was achieved by steering the yield of C₅H₇O₂+HO₂ towards C₅H₇O+OH 50% of the time. Other changes, like those required for the RO₂-RO₂ chemistry might be only relevant to this work. The 13% nitrate yield is also required for nitrates to match observed values in both isoprene and ISOPOOH experiments. There is considerable uncertainty in the yields of hydroxy acetone and glycolaldehyde under relatively long bimolecular lifetimes, an uncertainty that could not be resolved with our experiments. Further experiments should address the fate of the δ peroxy radicals which control the yields of most of the minor products.

Total production of HCHO and glyoxal is plotted in figure 3.28. The extensive changes to the mechanism made in this work do not have a large impact the total production of both of these species. However, in all cases, production of glyoxal and HCHO was increased. The yields of HCHO and glyoxal increase with NO_x which, for glyoxal, is the opposite of the trend expected by the AM3 mechanism.⁶⁵ Although production of these species increased, the changes in GEOS-Chem are not all positive. Substantial glyoxal losses are observed in the tropics where isoprene emissions dominate the production of this compound. In the same region HCHO concentrations increased as expected. Mechanistic differences between GEOS-Chem and the MCM as well as previously overestimated glyoxal yields can explain these results.

Glyoxal has the potential to contribute significantly to SOA. Our results suggest that low-NO_x oxidation of isoprene or its main products is not an unexpectedly large source of glyoxal. In fact,

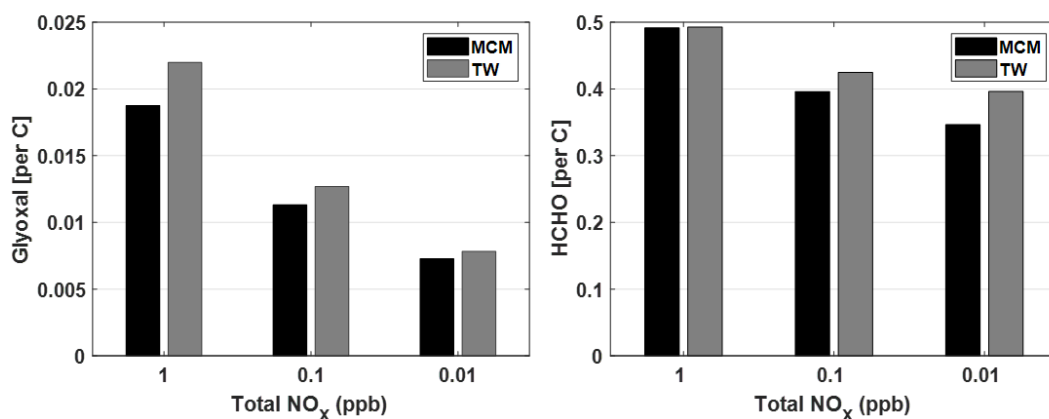


Figure 3.28: Changes to total HCHO and glyoxal production from isoprene oxidation. These model runs were performed until the oxidation of isoprene and its products was complete. NO_x was constrained so the total amount remained constant throughout the oxidation.

our results suggest that isomerization reactions are not significant contributors to glyoxal production. This implies that in places where isoprene dominates ambient concentrations of HCHO and glyoxal, RGF values that are higher than expected can be due to anthropogenic perturbations, inefficient hydroperoxide formation in the reaction of HO₂ and RO₂ or monoterpene influence.⁵⁵ We expect low RGF values to be correlated with longer RO₂ lifetimes, where glyoxal production is inhibited but not that of HCHO.

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