

Elucidating the Products and Kinetics of Bimolecular Alkene-Derived Peroxy Radical Reactions in the Lab and in the Field

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Sara Edinger Murphy

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Sara Edinger Murphy
ORCID: 0000-0002-8226-9446

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This thesis is dedicated to my father, James Edward Murphy, who nurtured in me
the curiosity about the world that inspired me to become a scientist.

*We're the wear on well-worn pages
where posterity retraces
the deeds of men
in bold relief*

- Women of the Ages (John Beaton)

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ABSTRACT

Although peroxy radicals, reactive compounds formed in the atmospheric oxidation of hydrocarbons, are primary drivers of atmospheric composition, several uncertainties remain with respect to their fates in both low and high NO environments. This thesis uses gas chromatography chemical ionization mass spectrometry (GC-CIMS) to identify and quantify the products of bimolecular peroxy radical reactions formed in both of these regimes in the lab and in the ambient environment. The first two chapters use laboratory experiments to probe the formation of a peroxide accretion product (ROOR) via peroxy radical self- and cross-reactions. In the first chapter, a method for studying the formation of the peroxide accretion product is developed and used to observe the formation of the accretion product of the ethene-derived hydroxy peroxy radical self-reaction. The self-reaction rate constant and the branching to the formation of the accretion product are measured, and the identity of the accretion product is confirmed by comparison to a synthesized standard. In the second chapter, the formation rate of the accretion product for a variety of small alkene-derived peroxy radical self-reactions is measured, and the observed relationship between peroxy radical structure and accretion product formation is discussed. Finally, the third chapter presents observations of organic nitrates formed via the reactions of biogenic and anthropogenic hydrocarbons in the Los Angeles urban atmosphere. The identities of several of these organic nitrates are confirmed by comparison to laboratory oxidation experiments, and the role these compounds play in the local nitrogen budget is discussed.

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TABLE OF CONTENTS

Acknowledgements	iv
Abstract	vii
Published Content and Contributions	viii
Table of Contents	viii
List of Illustrations	xi
List of Tables	xiv
Chapter I: Introduction	1
1.1 Background and Motivation	1
1.2 Mechanisms of Alkene Oxidation	2
1.3 Peroxy Radical Fates in High NO Environments	3
1.4 Peroxy Radical Fates in Low NO Environments	5
1.5 Techniques for Measuring the Products of Peroxy Radical Reactions	7
1.6 Research Results	8
Chapter II: Accretion Product Formation in the Self-Reaction of Ethene-Derived Hydroxy Peroxy Radicals	10
2.1 Introduction	10
2.2 Methods	13
2.3 Results and Discussion	22
2.4 Conclusions	34
Chapter III: Accretion Product Formation in the Self- and Cross-Reactions of Small Alkene-Derived Peroxy Radicals	35
3.1 Introduction	35
3.2 Methods	38
3.3 Results and Discussion	45
3.4 Conclusion	59
Chapter IV: A Census of Organic Nitrogen in the Los Angeles Atmosphere	60
4.1 Introduction	60
4.2 Methods	64
4.3 Results and Discussion	70
4.4 Conclusion	93
Chapter V: Conclusions and Outlook	94
5.1 Conclusions and Summary	94
5.2 Future Work	95
Bibliography	98
Appendix A: Supplementary Information for Chapter 1	109
A.1 Self-Reaction Scheme	109
A.2 Experimental Conditions	110
A.3 Additional Experimental Results	110

A.4 Reactions, Rate Constants, and Photolysis Frequencies in the Photo-chemical Box Model	119
A.5 Levenberg-Marquardt Optimization	120
A.6 GC Conditions	121
A.7 Peroxide Synthesis and NMR Analysis	122
A.8 Table of Results	127
A.9 Mass Balance in Oxidation Experiments	128
A.10 Calculated Polarizabilities and Dipole Moments	129
A.11 Calculation of Uncertainties	130
Appendix B: Supplementary Information for Chapter 2	132
B.1 GC Conditions	132
B.2 Sensitivities and Ion-Molecule Collision Rates	135
B.3 GC Transmission Efficiencies	136
B.4 GC Best-Fit Parameters	137
B.5 ID of Butanediol Stereoisomers	141
B.6 Tables of Results	142
B.7 Experimental Conditions	143
Appendix C: Supplementary Information for Chapter 3	145
C.1 Deuterium Exchange Experiments	145
C.2 Additional Results	146
C.3 Isoprene Hydroxy Nitrate Isomer Ratios	149
C.4 Experimental Conditions and GC Conditions	150
C.5 CIMS Sensitivities	153
C.6 Bootstrap Bet Fits of Ambient Data	153
Appendix D: Bringing a Lens of Equity to Geoscience Qualifying Examinations	156

LIST OF ILLUSTRATIONS

<i>Number</i>	<i>Page</i>
1.1 Major bimolecular reaction pathways of peroxy radicals.	4
2.1 Synthesis of alkyl peroxides 1-3	21
2.2 GC traces of products formed in ethene oxidation and synthesized standards.	24
2.3 ROOR and glycolaldehyde formation vs. ethylene glycol.	25
2.4 Least-squares fit of modelled Q to measured Q as a function of $\ln(F_{external})$	30
3.1 Representative chromatograms of ROOH and ROOR products formed in the high RO ₂ and high HO ₂ oxidation of 2-methylpropene.	47
3.2 Sample gas chromatograms of several important masses produced in the oxidation of cis-2-butene by OH in the presence of O ₂ and ethene.	50
3.3 Sample gas chromatograms of several important masses produced in the oxidation of propene by OH in the presence of O ₂ and ethene.	53
3.4 Measured values of $k_{3,2}\alpha_{3,2d}$ for the self-reactions of the ethene, methylpropene, propene, and cis-2-butene-derived peroxy radical systems.	55
3.5 The relationship between the self-reaction and cross-reaction rate constants for a variety of peroxy radical systems.	58
4.1 Simplified scheme showing the NO _x radical cycle and reactions leading to the formation of organic nitrogen during the daytime and the nighttime.	61
4.2 Daily conditions at the sampling site between August 28th, 2021 and September 5th, 2021 compared to concentrations of representative compounds measured with the Caltech CToF-CIMS.	65
4.3 Average diurnal profiles of representative masses from August 28th - September 5th.	71
4.4 The average total signal observed in the CToF-CIMS for a variety of nitrogen containing organic compounds.	73
4.5 Comparison between chromatograms at m/z 232 in the ambient chromatographic data and laboratory oxidation experiments.	74

4.6	Comparison between chromatograms at m/z 230 in the ambient chromatographic data and laboratory oxidation experiments.	77
4.7	Possible mechanism for the formation of the carbonyl compound observed at m/z 230 via oxidation of furan by NO ₃	79
4.8	Correlation matrix for all even masses.	81
4.9	Comparison of the relative sums of the normalized signals for the GC-HRToF and CToF-CIMS at each of the small alkene-derived hydroxy nitrate masses and the small alkene-derived nitrooxy hydroperoxide masses.	83
4.10	Ambient chromatographic data at m/z 220 compared with laboratory oxidation experiments.	85
4.11	Ambient chromatographic data at m/z 234 compared with laboratory oxidation experiments.	87
4.12	Ambient chromatographic data at m/z 236 compared with laboratory oxidation experiments.	90
4.13	Ambient chromatographic data at m/z 250 compared with laboratory oxidation experiments.	92
A.1	Peroxy radical self-reaction mechanism.	109
A.2	Decay of glycolaldehyde during photolysis experiment.	113
A.3	ROOR concentration before and after insertion of quartz and steel tubing.	114
A.4	Fraction of alkoxy radicals that proceed by reaction with O ₂	117
A.5	The ratio between glycolaldehyde and ethylene glycol as a function of the ratio of simulated RO ₂ to HO ₂ steady state concentration. . . .	118
A.6	¹ H NMR (400MHz, CDCl ₃) of compound 1	123
A.7	Infrared spectrum (Thin Film, NaCl) of compound 1	124
A.8	¹³ C NMR (100 MHz, CDCl ₃) of compound 1	124
A.9	¹ H NMR (400 MHz, CDCl ₃) of compound 2	125
A.10	Infrared spectrum (Thin Film, NaCl) of compound 2	126
A.11	¹³ C NMR (100 MHz, CDCl ₃) of compound 2	126
A.12	Mass balance in ethene oxidation experiments.	129
B.1	Comparison of chromatogram of m/z 175 formed in the oxidation of cis-2-butene during experiment performed on 10/9/2023 with chromatogram of 2,3-butanediol standard.	141
B.2	Plot of high resolution mass spectral data from the oxidation of cis-2-butene during experiment on 10/9/2023.	142

C.1	Comparison between the ratios of the signal at m/z 231 and the signal at m/z 230 during GCs with and without deuterium exchange.	145
C.2	Sum of ambient chromatograms at m/z 192 taken throughout the day on 08/29/2021 compared with laboratory OH oxidation of ethene. . .	146
C.3	Sum of ambient chromatograms at m/z 206 taken throughout the day on 08/29/2021 compared with laboratory NO ₃ and OH oxidation of propene.	146
C.4	Sum of ambient chromatograms at m/z 248 taken throughout the day on 08/29/2021 compared with laboratory oxidation experiments. . . .	147
C.5	Sum of ambient chromatograms at m/z 158 taken throughout the day on 08/29/2021 compared with chromatogram of 2-nitrophenol standard taken in the laboratory.	147
C.6	Comparison between signal observed at m/z 158 and m/z 220 in the CToF-CIMS.	148
C.7	Comparison between signal observed at m/z 248 and m/z 232 in the CToF-CIMS at night.	149
C.8	The ratio of the β hydroxy nitrate isomers throughout the campaign. .	149
C.9	Average contributions of isoprene and furan-derived products at m/z 230 observed during the RECAP-CA campaign during the daytime and nighttime.	154

LIST OF TABLES

<i>Number</i>	<i>Page</i>
2.1 Measured sensitivities and calculated relative ion-molecule collision rate coefficients.	20
2.2 Average photolysis frequencies of ROOR, ROOH, and glycolaldehyde in our atmospheric chamber.	27
2.3 Quantification of important $\text{HOCH}_2\text{CH}_2\text{OO} + \text{HOCH}_2\text{CH}_2\text{OO}$ reaction parameters and the sources of uncertainty.	29
2.4 Comparison between measured kinetic parameters in this and prior studies.	32
3.1 Measured $k_{\text{RO}_2+\text{RO}+2\alpha_{\text{ROOR}}}$ values.	56
4.1 Assignments of chromatographic peaks observed in ambient data at m/z 232.	75
4.2 Assignments of chromatographic peaks observed in the ambient data at m/z 230.	79
4.3 Assignments of ambient chromatographic peaks at masses that correspond to hydroxy nitrates primarily derived from small alkenes. . .	82
4.4 Assignments for ambient peaks corresponding to nitrooxy carbonyls derived from small alkenes in the GC-CIMS.	88
4.5 Assignments for peaks corresponding to nitrooxy hydroperoxides derived from small alkenes in the GC-CIMS.	91
A.1 Experimental conditions for ethene oxidation experiments.	110
A.2 Measured photolysis frequencies.	112
A.3 ROOR and ROOH photolysis results.	112
A.4 Bimolecular and termolecular reactions and rate constants used in photochemical box model.	119
A.5 Photolysis reaction rates used in photochemical box model.	120
A.6 Decay of products in the dark following photolysis.	120
A.7 Least squares Levenberg-Marquardt optimization parameters.	120
A.8 GC conditions in ethene oxidation experiments.	121
A.9 Experimental results of ethene oxidation experiments.	127
A.10 Calculated polarizabilities, dipole moments, and CF_3O^- -molecule collision rate coefficients for compounds of interest. $T = 298\text{K}$	130
B.1 GC conditions for methyl propene oxidation experiments.	132
B.2 GC conditions for cis-2-butene oxidation experiments.	133

B.3	GC conditions for propene oxidation experiments.	134
B.4	Calculated relative ion-molecule collision rate coefficients.	135
B.5	Calculated transmission efficiencies for various compounds in the 2m GC-CIMS.	136
B.6	Bootstrap best fit parameters for GC peaks in methylpropene and ethene oxidation experiments.	138
B.7	Bootstrap best fit parameters for GC peaks in cis-2-butene and ethene oxidation experiments.	139
B.8	Bootstrap best fit parameters for GC peaks in propene and ethene oxidation experiments.	140
B.9	Experimental results for experiments with methylpropene and ethene as precursors.	142
B.10	Experimental results for experiments with cis-2-butene and ethene as precursors.	143
B.11	Experimental results for experiments with propene and ethene as precursors.	143
B.12	Experimental conditions for experiments with ethene and methyl- propene as RO ₂ precursors.	143
B.13	Experimental conditions for experiments with ethene and cis-2-butene as RO ₂ precursors.	144
B.14	Experimental conditions for experiments with ethene and propene as RO ₂ precursors.	144
C.1	Experimental conditions for the ‘dark’ oxidation experiments.	150
C.2	Experimental conditions for the ‘light’ oxidation experiments.	150
C.3	GC conditions used in the ‘dark’ oxidation experiments.	152
C.4	GC conditions used in the ‘light’ oxidation experiments.	152
C.5	CToF sensitivities used in the analysis presented in Chapter 3.	153
C.6	Bootstrap best fit results for GC peaks observed in the ambient data at m/z 230 during the RECAP-CA campaign.	154
C.7	Bootstrap best fit results for GC peaks observed in the ambient data at m/z 234 during the RECAP-CA campaign.	155

LIST OF SCHEMES

1.1	Mechanism of OH addition to alkenes.	2
1.2	Mechanism of NO ₃ addition to alkenes.	3
3.1	Reaction scheme for the oxidation of 2-methylpropene by OH. . . .	46
3.2	Reaction scheme for the oxidation of cis-2-butene by OH in the presence of O ₂	49
3.3	Reaction scheme for the oxidation of propene by OH in the presence of O ₂	52

Chapter 1

INTRODUCTION

1.1 Background and Motivation

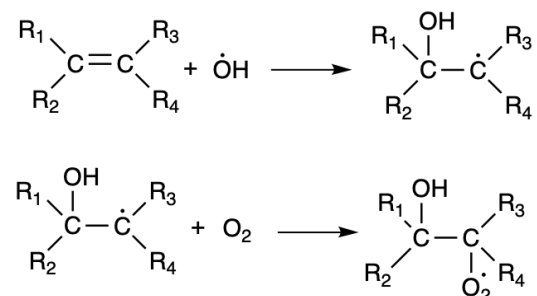
Atmospheric composition, one of the primary drivers of air quality and climate, influences the quality of life and longevity of communities worldwide. Poor air quality, characterized largely by high concentrations of ozone and particulate matter, is known to contribute to health problems such as cardiovascular and respiratory diseases, and, according to the World Health Organization (WHO), was linked to approximately 4.2 million excess deaths in 2019 (WHO, 2022; Cromar, Gladson, and Ewart, 2019; Gurjar et al., 2010; Pozzer et al., 2023). Further, changes in atmospheric composition impact radiative forcing, with some changes (such as increases in methane, O_3 , and CO_2) leading to increases in radiative forcing and some (such as increases in particulate matter) leading generally to decreases in radiative forcing (Isaksen et al., 2009). Often, these effects are nonlinear and complex, and the feedback between the climate and atmospheric composition, especially when it comes to particulate matter, remains poorly understood (IPCC, 2013). These radiative forcing effects are linked to changes in climate that increase the frequency of extreme climate events and resulting adverse health effects, with low income countries being the most vulnerable (Patz et al., 2005; Thiery et al., 2021; Sillmann et al., 2013; Harrington et al., 2016). The study of atmospheric composition and chemistry is, therefore, of critical importance to inform policy changes that seek to improve air quality and mitigate climate change.

Although the atmosphere is composed primarily of nitrogen (N_2) and oxygen (O_2), trace gases exert the greatest influence on air quality and climate (Seinfeld and Pandis, 2016). Non-methane hydrocarbons (NMHCs) are a subset of these trace constituents that play a role in the formation of O_3 and particulate matter. These hydrocarbons are emitted into the atmosphere via both anthropogenic and biogenic processes at a rate of approximately 1.3 gigatons per year and encompass several classes of compounds including alkanes, alkenes, terpenes, aromatic compounds and ethers, among others (Goldstein and Galbally, 2007). Unsaturated hydrocarbons constitute a significant proportion of these hydrocarbons, with alkenes in combination with alkanes accounting for up to 60% of total NMHCs in urban areas

and approximately 55% of the NMHCs globally emitted from vegetation (Atkinson, 1997a). Therefore, the oxidation and subsequent reactions of unsaturated and saturated hydrocarbons play an important role in the overall chemistry of NMHCs in the troposphere.

1.2 Mechanisms of Alkene Oxidation

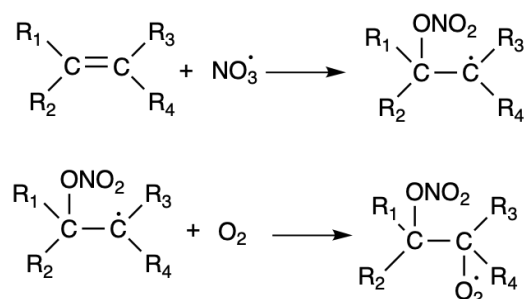
Upon emission into the troposphere, alkenes are oxidized by trace constituents such as the hydroxyl radical (OH), the nitrate radical (NO₃), and ozone (O₃) to form alkyl radicals. Oxygen (O₂) then rapidly adds to these alkyl radicals to form organic peroxy radicals (RO₂) (Atkinson, 1997a). During the daytime, OH is the primary oxidant, with the lifetimes of most alkenes with respect to reaction with OH on the order of hours, although for several alkenes reaction with O₃ may be competitive (Ziemann, 2011). The reaction of unsaturated hydrocarbons with OH proceeds either by hydrogen abstraction or OH addition to a double bond to form the alkyl radical. For the majority of alkenes, the OH addition pathway (Scheme 1.1) to form hydroxy peroxy radicals (hRO₂) is the predominant OH oxidation mechanism, with the hydrogen abstraction pathway generally accounting for <5% of the overall reaction of alkenes with OH (Atkinson, 1997a).



Scheme 1.1: The mechanism of OH addition to alkenes and subsequent formation of hydroxy peroxy radicals (hRO₂).

At night, when photochemistry is suppressed and OH concentrations are low, alkenes are primarily oxidized by the nitrate radical (NO₃), with lifetimes with respect to reaction with NO₃ on the order of minutes to days (Ziemann, 2011). NO₃, which forms via the reaction of NO₂ and O₃, does not contribute appreciably to oxidation during the daytime as NO₃ radicals undergo rapid photolysis, but is present in significant concentrations at night, with globally averaged nighttime concentrations of 5×10^8 molecules cm⁻³ (Ziemann, 2011). Analogously to reaction with OH, alkenes undergoing reaction with NO₃ may undergo NO₃ addition to form alkyl radicals. Hydrogen abstraction is generally negligible, and the commonly accepted

mechanism of alkene oxidation by NO_3 (Scheme 1.2) is addition to the double bond to form nitrooxy peroxy radicals (nRO_2) (Atkinson, 1997a).



Scheme 1.2: The mechanism of NO_3 addition to alkenes and subsequent formation of nitrooxy peroxy radicals (nRO_2).

The nRO_2 and hRO_2 formed in the oxidation of unsaturated hydrocarbons undergo a myriad of possible bimolecular reactions, including reaction with NO , HO_2 , or other RO_2 , which are summarized in Figure 1.1 (Orlando and Tyndall, 2012). Each of these reactions may lead to radical propagation, radical termination, or the formation of low volatility organic molecules, with each potential fate having vastly different implications for the overall chemistry of the atmosphere. Peroxy radicals may also undergo unimolecular reaction, including autooxidation, leading to the formation of highly oxidized organic molecules (HOMs) with volatilities that are often orders of magnitude lower than those of their respective parent compounds (Crounse, Nielsen, et al., 2013). The fate of peroxy radicals with respect to these potential reaction pathways is controlled by a combination of factors, including the structure of the peroxy radical, the time of day, the region, and the ambient conditions. However, while there has been significant progress in understanding each of these pathways and their atmospheric implications in recent decades, there remains significant uncertainty in the products of several of these possible pathways and thus in their atmospheric significance both regionally and globally (Lightfoot et al., 1992; Tyndall et al., 2001; Orlando and Tyndall, 2012; Jenkin, Valorso, et al., 2019).

1.3 Peroxy Radical Fates in High NO Environments

In regions where NO concentrations are high, such as urban centers with appreciable anthropogenic NO_x emissions, peroxy radicals will preferentially undergo bimolecular reaction with NO during the daytime (Orlando and Tyndall, 2012; Lightfoot et al., 1992). The major pathway of this reaction leads to the formation of an alkoxy

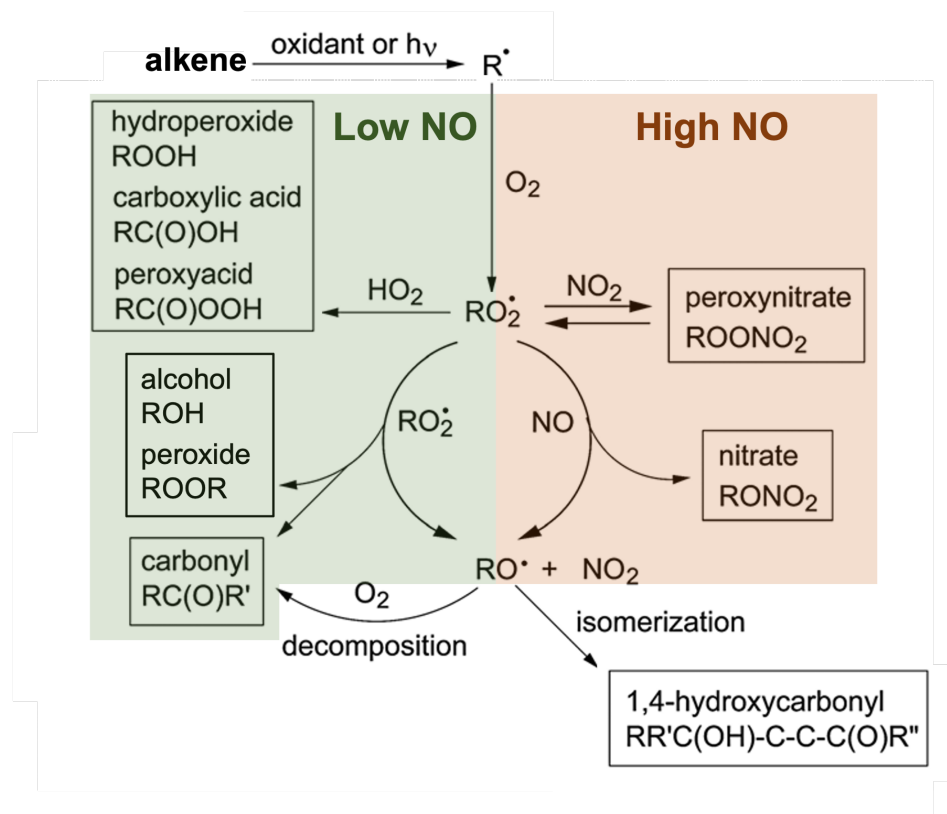


Figure 1.1: Major bimolecular reaction pathways of peroxy radicals, colored by their major reaction pathways in high NO (orange) and low NO (green) environments. Figure adapted from Ziemann and Atkinson, 2012.

radical (RO) and NO_2 eventually leading to the formation of O_3 , while a minor pathway leads to the formation of an organic nitrate ($RONO_2$). The relative branching to these potential reaction pathways varies widely across the suite of peroxy radicals present in the atmosphere, with the branching ratio to the formation of the organic nitrate ranging between 0.1-35% and largely depending on the stability of the $ROONO^*$ intermediate (Perring, Pusede, and Cohen, 2013). In the reactions of alkene-derived hRO_2 with NO , the branching to the formation of the hydroxy nitrate ranges between approximately 2% and 30%. The nitrate yield generally increases with increasing carbon number, increasing pressure, and decreasing pressure (Teng, Crounse, L. Lee, et al., 2015; Paulot, Crounse, et al., 2009; Perring, Pusede, and Cohen, 2013).

The formation of RO and NO_2 perpetuates a radical cycle that leads to ozone formation (Reactions 1.1a-1.1c).



The formation of an organic nitrate, however, terminates the radical cycle and (at least temporarily) sequesters NO_x . The sequestration of NO_x has a nonlinear effect on the production of ozone - where NO_x concentrations are high this decrease in NO_x leads to an increase in ozone production, while the opposite is true in regions with low NO_x . Further, the resulting organic nitrate is significantly less volatile than the precursor alkene, with the added $-\text{ONO}_2$ functionality decreasing the volatility by several orders of magnitude, and thus is more likely to partition into the particle phase and contribute to the formation of secondary organic aerosol (SOA) (Kroll and Seinfeld, 2008; Xu, Guo, et al., 2015; B. H. Lee, Mohr, et al., 2016). This is especially true of the hydroxy nitrates formed in alkene oxidation, as the addition of an $-\text{OH}$ group may further decrease the volatility of the parent alkene by an additional three orders of magnitude. Alternatively, RONO_2 may undergo deposition, photolysis, hydrolysis, or transport to more remote regions (Beaver et al., 2012).

Previous studies have highlighted the importance of including accurate representations of organic nitrate chemistry in global photochemical models, especially with respect to modelling of ozone and SOA concentrations (Romer Present, Zare, and Cohen, 2020; Browne and Cohen, 2012; Fisher et al., 2016; Bates and Jacob, 2019; Paulot, Henze, and Wennberg, 2012). However, these studies have also demonstrated that the impact of organic nitrate on global photochemistry remains uncertain due to the complexities of the fates, removal processes, and sources of these organic nitrates.

1.4 Peroxy Radical Fates in Low NO Environments

In regions with low NO concentrations, such as remote or forested regions, peroxy radicals are much more likely to undergo reaction with HO_2 or with other RO_2 (Orlando and Tyndall, 2012). This chemistry is becoming important even in some urban areas as NO concentrations continue to decrease due to emissions regulations (US EPA, 2014; Winkler et al., 2018). The reaction of alkene-derived peroxy radicals with HO_2 may lead to both radical propagating and radical terminating

channels (Jenkin, Valorso, et al., 2019):



Reaction 1.2a is the dominant pathways for simple alkyl radicals, and is generally still the predominant pathway for nRO_2 and hRO_2 , but Reactions 1.2b and 1.2c have been shown to contribute to the overall reaction of oxygenated peroxy radicals as well. Quantification of the relative importance of these pathways is essential, as while ROOH act as a temporary reservoir for HO_x , Reactions 1.2b and 1.2c recycle OH and thus perpetuate HO_x radical cycling. However, the branching ratios to each of these pathways remains uncertain for many classes of peroxy radicals, including many hRO_2 and nRO_2 , and the temperature dependence of these branching fractions also remains uncertain (Jenkin, Valorso, et al., 2019).

The reaction of RO_2 with other RO_2 (the self- or cross-reaction of RO_2) has traditionally been thought to proceed by three major pathways — the formation of two alkoxy radicals, the formation of an alcohol and a carbonyl, and the formation of a peroxide accretion product (Orlando and Tyndall, 2012). The formation of the accretion product (ROOR) was, until recently, largely ignored in the study of the RO_2 self-reaction. This is due, in part, to the general analytical challenge of observing and quantifying these peroxides as well as the seemingly unfavorable energetics of the proposed reaction mechanism, which suggests that the peroxy radicals form a tetroxide intermediate (ROOOOR), followed by the loss of the central O_2 atoms. The remaining alkoxy radicals then undergo an intersystem crossing (ISC) and recombine to form the peroxide (R. Lee et al., 2016; Hasan, Salo, et al., 2020; Hasan, Valiev, et al., 2021; Salo et al., 2022). This assumption was further supported by the fact that these dimers were not observed (or where they were observed, were observed in very small concentrations) in early studies of high RO_2 systems (Barnes, Becker, and Ruppert, 1993).

However, several studies within the last decade have provided evidence of the formation of the accretion products. Masses consistent with the ROOR, and with formation kinetics consistent with formation via the peroxy radical self-reaction, have been observed in the laboratory oxidation of α -pinene by OH, O_3 , and NO_3 (Berndt, Mentler, et al., 2018; Molteni et al., 2019; Bates, Burke, et al., 2022) and 1,3,5-trimethylbenzene by OH and O_3 (Berndt, Scholz, et al., 2018). Some of

these studies even saw formation of the accretion product at rates approaching the collision rate, suggesting that a significant fraction of the self-reaction may proceed via the formation of the ROOR, a drastic shift from previous assumptions (Berndt, Mentler, et al., 2018; Berndt, Scholz, et al., 2018). This result is atmospherically significant, as the ROOR is almost double the mass of the reactant peroxy radicals, leading to the formation of a low volatility product that is likely to play a role in the formation of secondary organic aerosol. In fact, products corresponding to the mass of the ROOR have been observed jointly in the gas and particle phases, in both the ambient environment and in the laboratory, supporting the hypothesis that the accretion product (if it forms) plays a role in aerosol formation and growth (B. H. Lee, Lopez-Hilfiker, et al., 2018; Bates, Burke, et al., 2022).

However, while these studies provided evidence for the formation of the accretion product, they did not confirm the identity of the ROOR. In these and other studies, dimerization products have also been observed at masses inconsistent with the ROOR, suggesting that other accretion mechanisms may explain observations of rapid dimer formation. In one study these dimers have been identified as esters that form in the particle phase, while an accretion mechanism involving the scission of the alkoxy radical in the intermediate has also been proposed to explain the observation of dimer esters in the gas phase (Kenseth et al., 2018; Peräkylä et al., 2023). Further research is needed to better constrain and understand accretion chemistry in high RO₂ systems, both in the particle-phase and in the gas-phase, and the role that gas-phase accretion mechanisms play in low NO environments. Additionally, as product studies have been performed for very few peroxy radical self-reactions with limited structural diversity, further work is needed to constrain the products and branching fractions of the RO₂ self-reaction (Jenkin, Valorso, et al., 2019).

1.5 Techniques for Measuring the Products of Peroxy Radical Reactions

The need for further studies of the products of bimolecular alkene-derived peroxy radical reactions across a variety of conditions, both in the laboratory and in the field, is complicated by the difficulty of measuring the multifunctional organic compounds formed in these reactions. Challenges involved in the measurements of these compounds include low sensitivities, instrumental losses of analytes, poor time resolution, lack of isomeric resolution, and fragmentation of analytes when using mass spectrometric methods (Vasquez, Allen, et al., 2018). The development of CF₃O⁻ chemical ionization mass spectrometry (CIMS) for use in field and laboratory studies was a significant step forward in addressing some of these challenges. This

method is highly sensitive to the multifunctional organic compounds of interest, can be integrated on a second time scale for excellent time resolution, has a limited range of sensitivity to these compounds, and is a softer ionization method that limits fragmentation (Crounse, McKinney, et al., 2006; Paulot, Crounse, et al., 2009). However, use of CF_3O^- CIMS alone does not address the problem of low concentrations of analytes, especially in the ambient environment, or the need for isomeric separation of these compounds. The GC-HRToF-CIMS, developed in this laboratory, addresses these concerns by enabling both for isomeric separation and preconcentration of trace analytes that might otherwise be in too low concentrations to be measured in the field (Vasquez, Allen, et al., 2018).

Throughout the work presented here, I use a combination of CF_3O^- CIMS and GC-HRToF-CIMS to analyze the formation of multifunctional organic nitrates formed in the reactions of alkene-derived peroxy radical reactions in the laboratory and in the field. In addition to addressing several concerns that are described above, the system used here is metal-free, limiting loss of the analytes to decomposition on metal surfaces. Further, since the instrument can separate individual isomers, I perform isomer-resolved measurements of each of the systems, which is essential for the systems studied here. Finally, the use of GC allows for definitive identification of compounds where possible.

1.6 Research Results

In this thesis, I probed some of the gaps in the literature with respect to the rates and products of these bimolecular peroxy radical reactions, both in the laboratory and in the ambient environment.

Chapters 1 and 2 describe the formation of accretion products in the peroxy radical self-reaction, and specifically the formation of the peroxide in the OH initiated oxidation of small alkenes. In Chapter 1, I develop a method for studying these products using observation of the ethene-derived ROOR and quantify the formation rate of the ROOR in this system. Further, I identify this product as the ROOR by comparison to synthesized standards. In Chapter 2, I extended this analysis to a suite of small alkene-derived peroxy radical self-reactions to probe the relationship between structure and accretion product formation.

Chapter 3 shifts focus to the reactions of peroxy radicals in high NO environments via the analysis of gas chromatographic data from the ambient Los Angeles urban atmosphere during the RECAP-CA campaign in the summer of 2021. Together with

others in my laboratory, we obtained a suite of gas-chromatography measurements of nitrogen containing organic compounds. We use these observations to identify the major nitrate products formed via these peroxy radical reactions and their role in the local NO_x budget.

Chapter 2

ACCRETION PRODUCT FORMATION IN THE SELF-REACTION OF ETHENE-DERIVED HYDROXY PEROXY RADICALS

Murphy, S. E. et al. (Mar. 2023). “Accretion Product Formation in the Self-Reaction of Ethene-Derived Hydroxy Peroxy Radicals”. In: *Environmental Science: Atmospheres*. ISSN: 2634-3606. DOI: [10.1039/D3EA00020F](https://doi.org/10.1039/D3EA00020F).

2.1 Introduction

Non-methane hydrocarbons are emitted to the atmosphere by both anthropogenic and biogenic processes at a rate of approximately 1.5 gigatons per year, making their chemistry an essential driver of tropospheric composition (Berndt, Mentler, et al., 2018). In the atmosphere, these compounds are oxidized by reaction with OH, NO₃, or O₃, often followed by addition of O₂ to form organic peroxy radicals (RO₂) (Berndt, Mentler, et al., 2018; Xu, Møller, Crounse, Otkjær, et al., 2019; Vasquez, Allen, et al., 2018; Orlando and Tyndall, 2012). RO₂ undergo a myriad of bimolecular and unimolecular reactions, including reactions that lead to radical termination or radical propagation. Some RO₂ reactions lead to the formation of highly oxidized organic molecules (HOMs) and subsequent particle formation and/or growth. To predict the effects of peroxy radical reactions on tropospheric chemistry, accurate measurements of the rates and products of their uni- and bimolecular reactions are required.

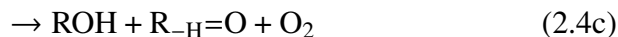
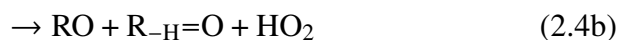
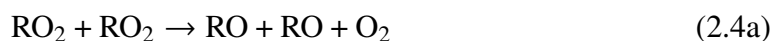
The diverse RO₂ reaction pathways yield products with differing effects on atmospheric chemistry and air quality. In environments with elevated NO, RO₂ react to form alkoxy radicals (RO) (Reaction 2.1a) and alkyl nitrates (RONO₂) (Reaction 2.1b). Reaction 2.1a generally propagates the radical chemistry leading to the formation of ozone (Reaction 2.2) (Orlando and Tyndall, 2012; Seinfeld and Pandis, 2016):



In low NO_x environments, RO_2 undergo unimolecular (Crounse, Nielsen, et al., 2013) or bimolecular reactions with HO_2 or other RO_2 . For β -hydroxyperoxy radicals, reaction with HO_2 leads to the formation of hydroperoxides (ROOH) (Reaction 2.3a) or other products such as RO (Reaction 2.3b) or a carbonyl, which in the case of the title reaction will be an aldehyde ($\text{R}_{-\text{H}}=\text{O}$) (Reaction 2.3c) (Orlando and Tyndall, 2012):



The RO_2 self- and cross-reactions include both radical propagating channels (2.4a,2.4b) and radical terminating channels (2.4c,2.4d). Reactions 2.4a, 2.4c, and 2.4d have been observed or proposed previously (Orlando and Tyndall, 2012), while Reaction 2.4b is proposed here to explain the excess yield of $\text{R}_{-\text{H}}=\text{O}$ relative to that of ROH , even in the absence of O_2 :



The rates and products of Reaction 2.1 in simple peroxy radical systems have been studied in detail and are generally well known (Orlando and Tyndall, 2012), while those of Reaction 2.3 are more uncertain. Reaction 2.3a is the dominant channel for most simple organic peroxy radicals reactions. In more substituted RO_2 , other channels, such as Reaction 2.3b and Reaction 2.3c, become non-negligible (Orlando and Tyndall, 2012; Praske et al., 2015).

The dynamics of Reaction 2.4 are complex as these pathways require significant electronic rearrangement and/or hydrogen shifts (R. Lee et al., 2016). The proposed mechanism of Reaction 2.4d requires an intersystem crossing (ISC) (R. Lee et al., 2016) and was previously believed to be unimportant to the chemistry of the troposphere (Orlando and Tyndall, 2012; Berndt, Mentler, et al., 2018) (see Appendix A.1). Recent studies utilizing chemical ionization mass spectrometry (CIMS) techniques, however, have detected compounds with molecular weights matching the expected products of Reaction 2.4d, generating renewed interest in quantifying the

formation of these peroxides (one of several compounds known as accretion products) (Berndt, Mentler, et al., 2018; Molteni et al., 2019; Kwan et al., 2012). In fact, several studies have found that for some RO_2 , Reaction 2.4d may proceed at rates approaching the collision rate, suggesting a drastic shift from previous assumptions (Berndt, Mentler, et al., 2018; Molteni et al., 2019; Berndt, Richters, Kaethner, et al., 2015). [While this manuscript was under peer-review, Yue et al., 2023 reported that a peroxide is produced in the $\text{RO}_2 + \text{RO}_2$ chemistry following H-abstraction from ethane at approximately 10% yield, using VUV photoionization mass spectrometry at 266 Pa and 298 K].

Investigation of the production of peroxides via Reaction 2.4d is of additional importance due to their potential to form secondary organic aerosol (SOA) (B. H. Lee, Lopez-Hilfiker, et al., 2018). Organic aerosols play an important role in climate forcing and have a negative impact on human health, but many routes leading to their formation are poorly quantified. Accretion products formed in Reaction 2.4d are much higher in carbon and oxygen numbers than the reactants and therefore have much lower volatility, increasing the likelihood that they condense from the gas phase to the particle phase (Seinfeld and Pandis, 2016). In both laboratory and field experiments, compounds with masses assigned to such accretion products have been observed in the aerosol and in the gas phase (B. H. Lee, Lopez-Hilfiker, et al., 2018; Berndt, Mentler, et al., 2018; Molteni et al., 2019; Kwan et al., 2012), confirming that their production can play an important role in the formation and growth of SOA. However, their identity and mechanism of formation remain unclear.

In this study, we revisit the self-reaction of the ethene-derived hydroxyperoxy radical, $\text{HOCH}_2\text{CH}_2\text{O}_2$. Previous studies have suggested that the formation of accretion products in this reaction is minimal (Barnes, Becker, and Ruppert, 1993). In contrast, we find that the branching fraction, $\alpha_{2.4d}$, is $23 \pm 5\%$. Using H/D exchange experiments, GC techniques, and synthesized standards, we provide evidence that the accretion product is dihydroxy diethyl peroxide ($\text{HOCH}_2\text{CH}_2\text{OOCH}_2\text{CH}_2\text{OH}$). We propose a new channel leading to direct HO_2 production, Reaction 2.4b. Finally, we constrain the rate coefficient for Reaction 2.4 from the ratio of products produced in this reaction to ROOH produced via Reaction 2.3a.

2.2 Methods

Experimental Design

Our goal in this investigation is to quantify the branching fractions and constrain the rate coefficient for the self-reaction of $\text{HOCH}_2\text{CH}_2\text{O}_2$ radicals formed following the sequential addition of OH and O_2 to ethene:



In the presence of ethene, the production of OH via photolysis of H_2O_2 in a 800 L FEP Teflon environmental chamber leads to the production of ethylene glycol (EG), glycolaldehyde (GA), dihydroxy diethyl peroxide (ROOR), and a hydroxy hydroperoxide, $\text{HOCH}_2\text{CH}_2\text{OOH}$. All experiments were performed at approximately 993 ± 10 hPa pressure and 294 ± 1 K.

OH is produced via the photolysis of H_2O_2 . Eight Sankyo Denki G40T10 254 nm lamps illuminated for 2 min yield a mean photolysis frequency for Reaction 2.6 of $3.0 \pm 0.5 \times 10^{-4} \text{ s}^{-1}$:



To determine the fraction of ethene reacted, we measured the OH exposure ($[\text{OH}] \times \text{time}$) from the decay of 2,3-butanediol during the oxidation period in several of our experiments. The primary product of this reaction, 2-hydroxy-3-butanone, is not made elsewhere in our reaction system. The rate coefficient for the reaction of OH with 2,3-butanediol has been reported by Bethel et al. using the relative rate method to be $2.4 \pm 0.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Bethel, Atkinson, and Arey, 2001). Bethel et al. measured this rate coefficient relative to that of OH + n-octane, for which they assumed a value of $8.67 \pm 0.17 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997b). Current recommendations suggest that the rate coefficient of OH with n-octane at 298 K is somewhat slower ($8.11 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Atkinson, 2003) so we use $2.25 \pm 0.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the OH + 2,3-butanediol rate constant in this analysis. Approximately 500 ppbv of butanediol was injected during these experiments. When 2,3-butanediol was not injected, we used a photochemical kinetic box model to determine the OH exposure. For the experiments with added butanediol, the modeled and measured OH exposure agree to within 30%. The total OH exposure during our experiments was between 0.8×10^9 - $4.3 \times 10^9 \text{ molecules cm}^{-3} \text{ s}$. To minimize secondary chemistry, the lights were turned off before 10% of the initial ethene had reacted, usually after 2 minutes.

Specific experimental conditions for each experiment used in this analysis are given in Appendix A.2 (Table A.1).

The branching fractions for Reaction 2.4 are determined from the formation of the products. Note that in this study, we use the following definitions, where j is the total number of possible pathways of Reaction X, α_{xi} is the branching fraction of pathway i of Reaction X, and k_x is the rate constant of a reaction X:

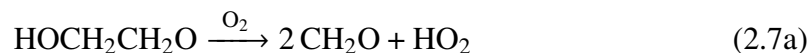
$$k_x = \sum_{i=1:j} k_{xi}$$

$$\alpha_{xi} = \frac{k_{xi}}{k_x}$$

$$k_{xi} = \alpha_{xi} k_x$$

To quantify the ratio of the radical terminating branching channels, $(\frac{\alpha_{2.4d}}{\alpha_{2.4c}})$, we measured the yields of ethylene glycol (EG) and dihydroxy diethyl peroxide (ROOR). In the absence of secondary chemistry, the ratio of their concentration is equal to the ratio of their branching fractions. Secondary losses of the products by reaction with OH is calculated to be minimal due to the small fraction of ethene oxidized during the experiment, and the main loss is photolysis. As described in Appendix A.3, we measured upper limits to the photolysis loss rates for EG, ROOH, glycolaldehyde (GA), and ROOR and find that these losses are also small (negligible for EG, less than 1% of GA, and less than 6% of ROOR and ROOH in a typical experiment). Additionally, we measured the wall loss rates for these compounds as a function of time and find that, over the time period of our experiments, these losses are negligible.

GA is produced in excess of EG in these experiments, consistent with significant additional sources beyond Reaction 2.4c. In 993 mbar of air, we attribute approximately half of the excess to the reaction of oxygen with the alkoxy radicals formed in Reaction 2.4a and Reaction 2.4b:



The fraction of the excess GA that results from Reaction 2.7b is well-explained using results from Orlando et al. (Orlando, Tyndall, et al., 1998) for experiments performed here under both much higher and lower $[\text{O}_2]$ as discussed in Appendix A.3. Theoretically, direct hydrogen atom elimination from the initially produce hot

alkoxy radical could also explain the excess glycolaldehyde production at low O_2 , but it is expected that C-C bond scission will be much faster. Thus, we tentatively attribute the remaining excess GA to Reaction (2.4b).

To further constrain the branching fractions and kinetics of Reaction 2.4, we perform a series of experiments varying the ratio of the formation rates of $HOCH_2CH_2O_2$ and HO_2 . In the absence of external sources, HO_2 is produced directly in Reaction 2.4b and indirectly via the subsequent chemistry of alkoxy radicals, e.g., decomposition (Reaction 2.7a) or via their reaction with O_2 (Reaction 2.7b). We increase the formation rate of HO_2 relative to RO_2 by adding CH_3OH to the chamber, which provides an external source of HO_2 independent of RO_2 :



A small amount of additional HO_2 is also produced in our experiments in Reaction 2.9:



As our independent variable, we define $F_{external}$, the ratio of the HO_2 produced externally to Reaction 2.4 via Reactions 2.8 and 2.9 to the amount of RO_2 produced via Reaction 2.5, where the k_R are the relevant reaction rate coefficients:

$$F_{external} = \frac{P_{HO_2,external}}{P_{RO_2}} = \frac{k_{R2.8}[CH_3OH] + k_{R2.9}[H_2O_2]}{k_{R2.5}[C_2H_4]} \quad (2.10)$$

When no methanol is added to the chamber and $k_{R2.9}[H_2O_2] \ll k_{R2.5}[C_2H_4]$, $F_{external}$ approaches zero and HO_2 is produced only as a result of Reaction 2.4. In this ‘high RO_2 ’ limit, significantly more RO_2 is produced in the chamber than HO_2 and, according to our box model simulations, more than 90% of the HO_2 reacts with RO_2 to produce $ROOH$ (the products of Reaction 2.3 will be discussed further in a later section). As such, the production of $ROOH$ provides a probe of the branching to the radical propagating channels in Reaction 2.4. To quantify this, we define the dependent variable Q :

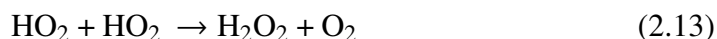
$$Q = \frac{[ROOH]}{[HOCH_2CH_2OH] + [ROOR]} \quad (2.11)$$

In the limit where $F_{external} \rightarrow 0$, Q is a measure of the ratio of the branching fractions of the radical propagating channels to the radical terminating channels:

$$Q_{high\ RO_2\ limit} = \frac{2(\alpha_{R2.4a} + \alpha_{R2.4b})}{\alpha_{R2.4c} + \alpha_{R2.4d}} \quad (2.12)$$

where the factor of 2 in the numerator arises because Reactions 2.4a and 2.4b, including the subsequent reactions of the alkoxy radicals, each produce two HO₂. Therefore, the y-intercept of Q as a function of $F_{external}$ provides a constraint on the ratio of the radical propagating and radical terminating channels of Reaction 2.4.

To further constrain the kinetics of Reaction 2.4, we explore the ‘high HO₂ limit’, where $F_{external} \gg 1$. In this limit, nearly all the OH produced from the photolysis of H₂O₂ reacts via Reactions 2.8 and 2.9 to produce HO₂. Because the formation rate of HO₂ greatly exceeds that of RO₂, the HO₂ self-reaction is its main loss:



while the main loss of RO₂ is its reaction with HO₂ (Reaction 2.3).

Because, as follows from Equation 2.11:

$$Q = \frac{k_{R2.3}[HO_2][RO_2]}{k_{R2.4}(\alpha_{R2.4c} + \alpha_{R2.4d})[RO_2][RO_2]} \quad (2.14)$$

and the ratio of [HO₂] to [RO₂] in the high HO₂ limit is determined by the ratio of their production multiplied by the ratio of their lifetimes,

$$\frac{[HO_2]}{[RO_2]} = F_{external} \frac{k_{R2.3}}{2k_{R2.13}}, \quad (2.15)$$

in the high HO₂ limit, Q is a sensitive measure of the ratio of $k_{R2.3}^2$ to $k_{R2.4}$:

$$Q_{\text{high } HO_2 \text{ limit}} = \frac{1}{2k_{R2.13}} \times \frac{k_{R2.3}^2}{k_{R2.4}(\alpha_{R2.4c} + \alpha_{R2.4d})} \times F_{external}. \quad (2.16)$$

In our experiments, $F_{external}$ ranges from 0.04 to 4.5. The lower limit results from the use of H₂O₂ as the OH precursor — some external HO₂ is produced from its reaction with OH even in the absence of methanol addition — while the maximum $F_{external}$ is limited by insufficient production of RO₂ products and the resulting poor quantification of Q.

The limiting behaviors described by Equations 2.12 and 2.16 are useful for designing the experimental methods, for quantifying initial estimates of our parameters, and to perform sensitivity analyses to estimate uncertainty. However, to formally estimate the branching fractions and the rate coefficients, we use a box model that includes all the reactions described above. The complete set of reactions and rate constants used in the box model is given in Appendix A.4 (Tables A.4, A.5, and A.6). The difference between the box model output (the value of Q as a function of $F_{external}$) and our

data is minimized using a least-squares Levenberg-Marquardt (LM) algorithm to optimize the relevant branching fractions and the ratio of the rate coefficients of Reaction 2.4 to Reaction 2.3. The LM constraints used are provided in Appendix A.5 (Table A.7).

Instrumentation

All measurements were performed with a high-resolution time-of-flight chemical ionization mass spectrometer (HRTof-CIMS) using CF_3O^- as the reagent ion. The instrument also contains a metal-free, low pressure gas chromatograph (GC). This instrument has been described in detail elsewhere (Vasquez, Allen, et al., 2018), but a brief summary of the critical components is given here. The HRTof-CIMS samples either from the output of the GC or directly from the experimental chamber (direct sampling mode). The CF_3O^- reagent ion is produced by passing dilute CF_3OOCF_3 gas in N_2 through a tube coated with polonium-210. Sampled chamber gas passes at 180 sccm through a Teflon-coated critical orifice into a Teflon-coated glass flow tube maintained at a pressure of 35 mbar, where it is diluted with N_2 and mixes with the flow from the ion source. Reagent ions then react with analytes from the chamber to form product ions. CF_3O^- reacts with many multifunctional organic compounds at the ion-molecule collision rate to yield cluster ions at the mass of the reagent ion (85) plus the mass of the analyte. For example, ethylene glycol, with a molecular weight of 62, is detected at m/z 147. These ion clusters enter the mass spectrometer through a pinhole and a conical hexapole ion guide. In addition to forming clusters, hydroperoxides produce a small fraction (a few %) of characteristic fragmentation ions at m/z 63 and m/z 81, enabling identification of such analytes. For some analytes (e.g., H_2O_2) the cluster ions are not well bound, such that not all collisions result in a stabilized ion cluster. For these analytes, the resulting sensitivities are therefore lower than estimated based on the ion-molecule collision rate (Crounse, McKinney, et al., 2006). The HRTof-CIMS collected ion signals ranging between m/z 19 and m/z 396 at a mass resolving power of approximately 3000 ($m/\Delta m$).

The GC consists of a 1-meter fused silica column (Restek RTX-1701) cooled via evaporation and expansion of liquid CO_2 and warmed with resistive heating elements connected to a Watlow temperature controller. The sample is diluted by a flow of dry N_2 before being cryotrapped on the head of the column at a temperature of -40°C or below for between 5 and 10 minutes. The specific trapping temperature, time, and dilution for each experiment are chosen to maximize the amount of analyte

collected while minimizing the water trapped. When trapping is complete, 5 sccm N_2 flows through the column while the temperature of the GC steadily increases at a predetermined ramp rate chosen to best separate analytes of interest in the minimum amount of time. The elution stream from the GC oven is combined with a 200 sccm flow of nitrogen and routed to the mass spectrometer flow tube. Specific conditions for the experiments discussed in this paper are given in Appendix A.6 (Table A.8).

Reagent Preparation

H_2O_2 (30% by mass, Macron Fine Chemicals) was pipetted into a three-way glass vial and weighed for accurate mass determination. Dry air was then passed through the vial into the experiment chamber at 20 SLM until all the reagent was evaporated, as verified by reweighing the vial after injection. 2,3-butanediol (98%, Sigma-Aldrich) was added to the chamber in a similar manner.

Ethene ($\geq 99.5\%$, Sigma-Aldrich) and methanol ($\geq 99.9\%$, Sigma-Aldrich) samples were prepared in 500-mL glass bulbs using manometry. The bulb was attached to a vacuum/ N_2 system and reagent source, and the desired concentration of ethene and methanol was obtained via serial dilution measured with pressure sensors (MKS 1000 and 10 Torr baratron pressure transducers). Concentrations were also determined using FTIR measurements by fitting spectra to absorption cross sections from the PNNL IR Database (Sharpe, Sams, and Johnson, 2002). The manometry and IR determinations agreed to better than 10%.

CIMS Calibration

Quantification of the various RO_2 reaction products requires knowledge of their sensitivity in the CIMS instrument. The Caltech CIMS implementation uses a transverse ionization approach where the CF_3O^- reagent ions travel across the 35 mb gas mixture flow in approximately 5 ms before entering the mass filter. The short reaction time of the reagent ions with the analytes yields a sensitivity for each compound that is proportional to: the ion-molecule collision rate with the analyte, the fraction of such collisions that result in ion products, the transmission efficiency of such ions, and whether there is fragmentation, all modulated by the number of CF_3O^- produced in the polonium source. As the fraction of reagent ions, here primarily CF_3O^- and its clusters with H_2O and H_2O_2 (observed at m/z 85, 103, and 119, respectively), that react with the analytes is small, we first normalize the signals at the cluster mass (e.g., the counts at m/z 163 for the hydroxyhydroperoxide) by the sum of signal for the reagent ions. Because the number of reagent ions is very high,

to remain in a linear counting regime, we use the reagent ion signal for the sum of the minor isotopologues at $m/z+1$ (e.g., 86 for CF_3O^-). So, the sensitivities listed in Table 2.1 below are normalized by the sum of m/z 86 + m/z 104 + m/z 120. These normalized signals are proportional to concentration of each analyte ionized in the flow.

To determine the sensitivity of the CIMS to ethylene glycol, we used two methods to produce gas phase standards. In the first, ethylene glycol (Sigma-Aldrich) was evaporated into a 200-L Teflon bag, which was then attached to an FTIR and a flow dilution system in series with our GC-CIMS. The concentration of EG in the Teflon bag was quantified using the FTIR and cross sections from the PNNL IR Database as air from the 200 L bag flowed through a 19 cm pyrex FTIR cell with CaF_2 windows at a rate of 484 sccm. The uncertainty in the FTIR cross sections is estimated to be $\leq 7\%$. Following the FTIR cell, a subsample (34 sccm) was diluted into a 2 SLM nitrogen flow yielding EG concentrations of approximately 1 ppmv which was directed into the CIMS instrument. In the second method, we prepared a known concentration of EG by flowing 20 sccm of air over a diffusion vial maintained at 30°C . The diffusion vial containing EG was regularly weighed. The mass loss rate of EG over time, and the flow rate in the CIMS flow tube were used to calculate the mixing ratio of EG in the flow tube. The sensitivity calculated using these two methods agrees within 8%. The sensitivity using the diffusion vial method was repeated often and the average is listed in Table 2.1.

To estimate the sensitivity for the other RO_2 reaction products, we calculate their ion-molecule collision rate relative to that of EG. CF_3O^- binds strongly to most multifunctional organic compounds (Hytinen et al., 2018) and as such, the fraction of each product ionized depends linearly on the ion-molecule collision rate. For some analytes, such as H_2O_2 , the ion-molecule complex binding energy is small, and not all collisions lead to stabilized product ions. This dissociation is diagnosed by evaluating the sensitivity as a function of temperature and water vapor. For weakly bound clusters, the sensitivity decreases as a function of temperature and generally has a complex behavior as a function of water — sometimes increasing at low concentrations as the water chaperone increases cluster formation, before decreasing at high water concentrations due to ligand switching (Crounse, McKinney, et al., 2006; Hytinen et al., 2018). For the product clusters described in this work, we find that the sensitivity is largely insensitive to temperature and both water and H_2O_2 , consistent with high stability for the ion clusters. Even for well bound clusters,

Table 2.1: Measured sensitivities and calculated relative ion-molecule collision rate coefficients. Errors are the standard deviations of replicate measurements or, in the case of 2,3-butanediol and 2-hydroxy-3-butanone where only one measurement was performed, the error is determined by propagation. ^aSignals are normalized to the signal of the ¹³C isotope of the reagent ion (m/z 86 + m/z 104 + m/z 120). ^bRelative to ethylene glycol. ^cThe ratio of sensitivity to ethylene glycol is lower than the ratio of the ion-molecule collision rate coefficients due to incomplete stabilization of collisions (Crounse, McKinney, et al., 2006).

Compound	Measured Sensitivity (cts/ppTV) ^a	Calc. CF ₃ O ⁻ -molecule collision rate ^b
Ethylene glycol	$2.5 \pm 0.2 \times 10^{-4}$	1
H ₂ O ₂ ^c	$1.65 \pm 0.06 \times 10^{-4}$	0.94
2,3-butanediol	$2.8 \pm 1.6 \times 10^{-4}$	1.02
2-hydroxy-3-butanone		1.29
Glycolaldehyde	$2.7 \pm 0.2 \times 10^{-4}$	1.08
HOCH ₂ CH ₂ OOCH ₂ CH ₂ OH		1.05
HOCH ₂ CH ₂ OOH		1.08

the efficiency of formation of CF₃O⁻ clusters following collision can be less than unity if they fragment into smaller ions. The data obtained with the GC enables us to quantify this fragmentation for each analyte, and we observe very little such fragmentation for the species reported here. The hydroxyhydroperoxide (m/z 163) produces a very small signal at m/z 145 (< 2%) and m/z 63+81 (2-3%). (The latter two ions are diagnostic of organic hydroperoxides (Paulot, Crounse, et al., 2009; St. Clair et al., 2014; Crounse, Paulot, et al., 2011)). Given the size and stability of the ion products and the lack of significant fragmentation, we expect that for all the RO₂ reaction products, the sensitivity of each for its CF₃O⁻ cluster will scale with the ion-molecule collision rate to within $\pm 20\%$.

To calculate the ion-molecule collision rate, we use the method of Su et al. (1982) together with calculated dipole moments and polarizabilities using quantum calculations (Garden et al., 2009). The calculated ion-molecule collision rates, relative to that for ethylene glycol are listed in Table 2.1.

Peroxide Synthesis

Previous studies of the formation of accretion products have observed compounds at the mass of the peroxides (ROOR) using CIMS techniques (Berndt, Mentler, et al., 2018; Molteni et al., 2019; Berndt, Richters, Kaethner, et al., 2015), but the identity of these products has not been typically confirmed. Studies by Kenseth et al. (2018)

have, for example, shown that accretion products produced in the ozonolysis of pinenes are not peroxides and do not form in the gas phase. Here, a method for the synthesis of a standard for the C4 dihydroxy peroxide for comparison to our oxidation products is outlined.

General Information. Caution: Although no explosions were experienced in this work, organic peroxides are potentially hazardous compounds and must be handled with great care: Avoid direct exposure to strong heat or light, mechanical shock, oxidizable organic materials, or transition-metal ions. A safety shield should be used for all operations involving H_2O_2 .

Unless otherwise stated, reactions were performed in flame-dried glassware under ambient conditions using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Reagents were purchased from commercial sources and used as received. Reaction temperatures were controlled by an IKA Mag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (250 μm) and visualized by UV fluorescence quenching, potassium permanganate staining, or p-anisaldehyde staining. Silicycle SiliaFlash P60 Academic Silica gel (particle size 40–63 μm) was used for flash chromatography. Preparative HPLC was performed using an Agilent 1200 HPLC system equipped with an ACE C18 column (5 μm , 21.2 mm $\times$ 250 mm). ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 500 (500 and 125 MHz, respectively) spectrometer and are reported in terms of chemical shift relative to CHCl_3 (δ 7.26 and 77.16 ppm, respectively). Data for ^1H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant, integration). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. IR spectra were obtained from thin films deposited on NaCl plates using a Perkin Elmer Spectrum BXII spectrometer and are reported in wavenumbers (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm) using a 100 mm path-length cell. All of the spectral data can be found in Appendix A.7.

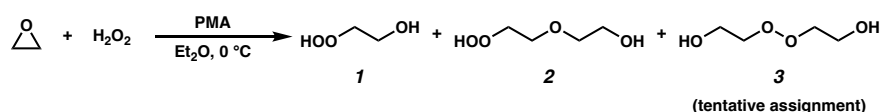


Figure 2.1: Synthesis of alkyl peroxides **1-3**.

Alkyl Peroxides 1-3. Compounds were prepared according to a modified literature procedure (Li, Hao, and Wu, 2009). To a flame dried 25 mL round bottom flask was added ethereal H_2O_2 (Li, Hao, Q. Zhang, et al., 2009) (1M solution, 10 mL, 10 mmol, 1.0 equiv). This solution was brought to 0 °C, and ethylene oxide was bubbled into the solution for 30 s. PMA (phosphomolybdic acid, 182 mg, 0.1 mmol, 0.01 equiv) was added and the reaction mixture was stirred at 0 °C for 20 min. After 20 min, H_2O_2 remained by TLC analysis (100% ethyl acetate, visualized with p-anisaldehyde). Ethylene oxide was again bubbled into the solution for 30 s, and an additional 500 mg (0.27 mmol, 0.027 equiv) of PMA was added. The reaction mixture was stirred for another 1 h at 0 °C, at which point TLC indicated consumption of H_2O_2 . The reaction mixture was pushed through a short silica plug and concentrated. Analysis of the crude clear residue using GC-CIMS showed the presence of a compound with $m/z = 163$, eluting at 31 °C, and two compounds with $m/z = 207$, eluting at 52 °C and 64 °C, respectively (Figure 2.2). All chromatograms were run under the same conditions as those described in the Appendix A.6 for the oxidation experiments, with at least 5 minutes of trapping time at -45 °C.

The clear residue was purified via preparatory TLC (5% methanol/ethyl acetate, visualized with p-anisaldehyde). All major bands were collected and were subjected to GC-CIMS analysis. Only two compounds were observed via GC-CIMS analysis: one major compound at m/z 163 and one major compound at m/z 207 (Figure 2.2). The chromatograms of both of these compounds contain daughter ions characteristic of -OOH functional groups (m/z 63 and m/z 81).

The two isolated products were identified to be hydroxyhydroperoxide **1** (20.0 mg, 3% yield, colorless oil) and ether **2** (5.4 mg, less than 1% yield, colorless oil). We believe that peroxide **3** forms under the reaction conditions, as a second peak at $m/z = 207$ is observed in the crude reaction mixture, but is not stable to isolation. Additionally, compound **3** elutes at the same temperature as the putative accretion product in our oxidation experiments.

2.3 Results and Discussion

The Identity of the Accretion Product

Although several recent studies have reported formation of accretion products in oxidation experiments of organic compounds (Berndt, Mentler, et al., 2018; Molteni et al., 2019; Berndt, Richters, Kaethner, et al., 2015), the identity of these compounds remains generally unclear. For example, Kenseth et al. (2018) have recently

shown that accretion products formed in the ozonolysis of α - and β -pinene arise not directly in the gas phase but rather from heterogeneous reactions of alcohols and (likely) peroxides produced via O_3 and OH chemistry, respectively. Here, in this simplest of systems, we show that the accretion product is likely an organic peroxide, $HOCH_2CH_2OOCH_2CH_2OH$. As shown in Figure 2.3, across all our experiments from those with minimal HO_2 chemistry to those dominated by such reactions, the yield of the accretion product closely tracks the yield of ethylene glycol, a unique gas-phase product of the self-reaction of $HOCH_2CH_2OO$, suggesting that it is also produced in the gas phase via this self-reaction.

Shown in the first panel of Figure 2.2 are gas chromatograms of the products formed in our ‘high RO_2 ’ experiments. Due to its high vapor pressure, glycolaldehyde is not efficiently trapped on the column. All the other products — ethylene glycol, the hydroperoxide, and the accretion product — are efficiently collected, separated, and detected at their CF_3O^- cluster m/z . The average GC transmission efficiencies of all of these species were between 90–100%.

Three plausible molecules with the formula $C_4O_4H_{10}$ can be postulated to form in the gas-phase chemistry of $HOCH_2CH_2OO$, and in the condensed-phase synthesis, considering the starting materials: a hydroperoxyhydroxyether, a dihydroxyperoxide, and a triol ether. The last compound can be distinguished from the first two by the number of readily exchangeable hydrogens. To rule out the triol ether, we added D_2O to the GC effluent and, as shown in panel b of Figure 2.2, ethylene glycol and the C_2 hydroxyhydroperoxide shift up 2 m/z , consistent with two exchangeable hydrogens. Likewise, the accretion product shifts up 2 m/z . No +3 m/z isotopologues are observed. As such we eliminate consideration of the triol as a plausible structure for the accretion product.

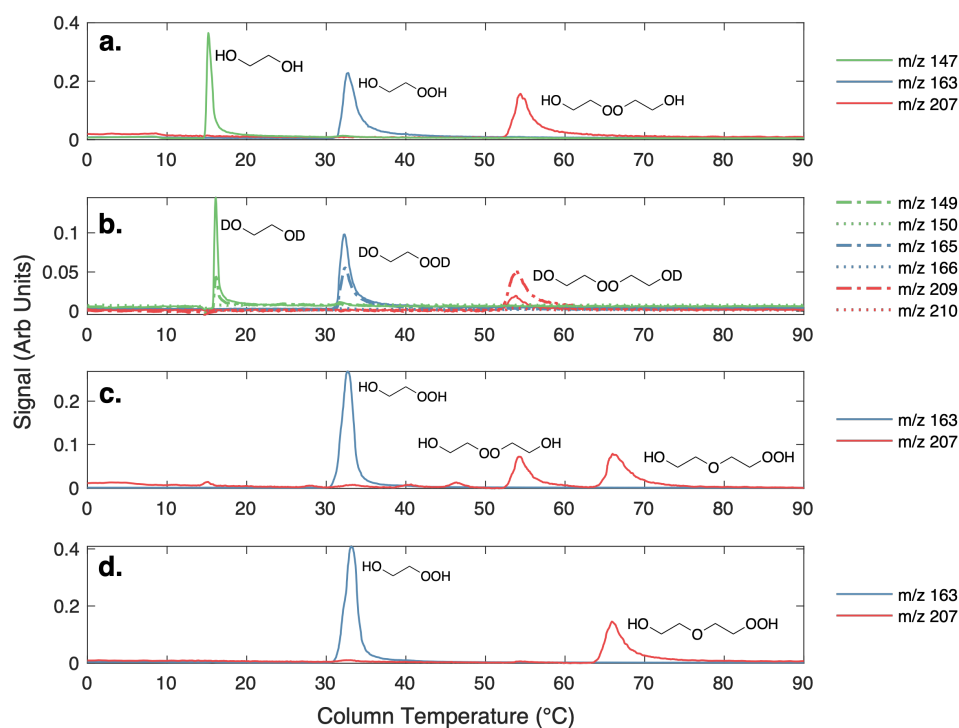


Figure 2.2: GC traces of products formed in ethene oxidation and synthesized standards. **a.** GC traces of three products of the ethene oxidation experiments: ethylene glycol (m/z 147), accretion product (m/z 207), and ROOH (m/z 163). **b.** GC traces with D₂O added to flow tube. Dashed lines are signals at m/z + 2 for each product shown in a, and dotted lines are the signals at m/z + 3 for each product. Solid lines are signals at each original product m/z. **c.** GC traces of m/z 163 and m/z 207 from the synthesized standard prior to prep TLC purification. **d.** GC traces of m/z 163 and m/z 207 from the standard after purification by preparatory TLC.

Also shown in Figure 2.2 (panels c and d) is the chromatograph of the synthetic products from the liquid phase condensation of the hydroperoxide (as described above). Two compounds at the m/z of the accretion product (m/z 207, mw 122) are observed in the crude mixture, while only one C₄O₄H₁₀ compound is stable to prep TLC separation. The isolated compound eluting at approximately 65°C is identified as the hydroperoxy hydroxy ether, HOCH₂CH₂OCH₂CH₂OOH, based on the ¹H and ¹³C NMR spectra (see SI) and on the observed fragmentation of m/z 207 to m/z 63 and m/z 81 in CF₃O⁻ CIMS, fragments characteristic of hydroperoxides (Paulot, Crounse, et al., 2009; St. Clair et al., 2014). The first peak, the peroxide, elutes at the same temperature as the accretion product formed in the gas-phase experiments. Therefore, we conclude by elimination that the accretion product formed in the

gas-phase ethene oxidation experiments is likely the dihydroxyperoxide (ROOR).

Product Branching Fractions

To calculate the branching fractions of the self-reaction, we quantify the closed-shell end products of these reactions (with the exception of formaldehyde, which does not cluster with CF_3O^-). Reaction 2.4 directly produces three products: ethylene glycol, glycolaldehyde, and the accretion product (ROOR).

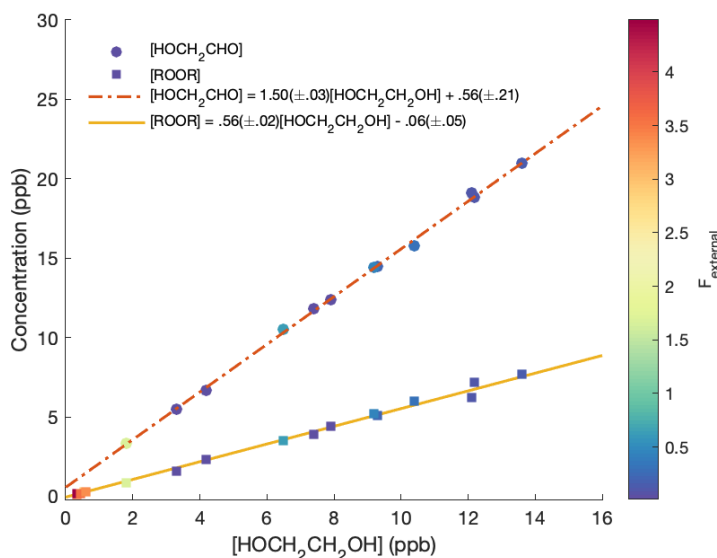


Figure 2.3: ROOR and glycolaldehyde formation vs. ethylene glycol. Dashed and solid lines are linear fits to the data, with slopes of 0.56 ± 0.02 and 1.50 ± 0.03 for ROOR and glycolaldehyde, respectively.

Shown in Fig. 2.3 are the concentrations of ROOR and glycolaldehyde as a function of the concentration of ethylene glycol. The points are colored by the value of F_{external} . The observed yield of ROOR relative to EG is 0.56 ± 0.02 . In 21% O_2 at 993 hPa, the yield of GA relative to EG is 1.50 ± 0.03 . The ratio of the ROOR to EG is independent of F_{external} . The ratio of GA to EG increases at the highest F_{external} as a result of secondary chemistry of the ROOH, and therefore we do not include these points in the above fit (see Appendix A.3).

Absent secondary chemistry, the ratio of the product yields equals the ratio of their production. To accurately determine the ratio of their production, however, secondary losses must be considered. Here, this potentially includes the photolysis of the peroxide product (ROOR), the hydroperoxide (ROOH), and glycolaldehyde. We

measured the upper limit of the photolysis rate of these compounds in our chamber as follows: after synthesizing them in the gas phase via an ethene oxidation experiment in the high RO₂ limit, we evacuated the chamber through a coil of Teflon tubing submersed in an ethanol/liquid nitrogen bath maintained at approximately -30°C, trapping the low volatility products while allowing the remaining ethene and high volatility products to be pumped away. We then flushed out the chamber with clean air and returned the contents of the trap to the Teflon chamber by flowing dry air back through the trap at room temperature (294 K). Finally, we added 50 ppmv methanol to convert any OH produced by subsequent photochemistry to HO₂, thereby isolating the loss due to photolysis. We then turned on the UV lights and measured the loss rates of the relevant compounds. During a typical 2 min photolysis experiment, we calculate that 1% of the GA is photolyzed and at most 6% of the ROOR was lost. Photolysis of the hydroxyhydroperoxide (ROOH) results in a maximum loss of a few percent. However, these measured photolysis rates are an upper limit to the loss via photolysis, as there may be additional secondary losses during these photolysis experiments - we expect that the true photolysis rates of ROOR and ROOH are likely closer to that of hydrogen peroxide. Therefore, in our subsequent analysis, we assume that over the 120 s time period of our experiments, the average photolysis frequency for the ROOR and ROOH is $3.0 \times 10^{-4} \text{ s}^{-1}$. If instead we use the upper limit to the photolysis frequencies, the estimated branching ratios to ROOR and ROOH increase by approximately a factor of 1.05. We observe no significant photolysis of ethylene glycol over the experiment timescales. In addition to secondary losses, GA is also formed via the reaction of OH with ROOH and EG and via photolysis of ROOH and subsequent reaction of O₂ with the generated RO. This chemistry is only significant when ROOH is much larger than GA (e.g., at high F_{external} (see Appendix A.3)).

Accounting for the photolysis losses and glycolaldehyde production, we find that the ratio of the production of ROOR and GA to ethylene glycol are 0.57 ± 0.10 and 1.55 ± 0.20 , respectively, where the uncertainty is derived primarily from the uncertainty in the relative calibration of the CIMS for these compounds. In the first-generation chemistry of this reaction system, Reaction 2.4 is a unique source of the accretion product and EG, so the ratio of their production is equal to the ratio of the branching in Reaction 2.4 ($\frac{\alpha_{2.4d}}{\alpha_{2.4c}}$). GA, however, is also produced in the subsequent reactions of the alkoxy radical and O₂ (Reaction 2.7b) (Orlando, Tyndall, et al., 1998) and, speculatively, via a radical propagating reaction, Reaction 2.4b. There may be additional GA formed via Reaction 2.3. The formation of GA

Table 2.2: Average photolysis frequencies of ROOR, ROOH, and glycolaldehyde in our atmospheric chamber with 8 lamps ($\lambda = 254$ nm). The measurements of ROOR and ROOH are upper limits of the photolysis loss. Reported uncertainties are the uncertainties in slopes fitted to the decay of these compounds as described in the SI. The literature cross sections are determined from $\ln$ of the intensities.
^aKeller-Rudek et al., 2013

Compound	Average Photolysis Frequency (10^{-4} s^{-1})	Literature Cross Section ^a ($\text{cm}^2 \text{ molec}^{-1}$)
HOCH ₂ CH ₂ OOCH ₂ CH ₂ OH	$< 6.1 \pm 0.8$	
HOCH ₂ CH ₂ OOH	$< 5.2 \pm 0.9$	
HOCH ₂ CHO	1.7 ± 0.05	$4.0 \pm 0.3 \times 10^{-20}$
H ₂ O ₂	3.0 ± 0.5	$7.0 \pm 1.0 \times 10^{-20}$

in these experiments is discussed further below.

Glycolaldehyde Formation

As shown in Figure 2.3, the yield of glycolaldehyde is consistently higher than the yield of ethylene glycol across our experiments. This is true even when oxygen is reduced to 1% of the total volume to minimize the extent of Reaction 2.7b (see SI Appendix C). This observation is consistent with prior studies of GA formation in the ethene oxidation system. In the FTIR study of the title reaction by Barnes et al. (Barnes, Becker, and Ruppert, 1993), for example, GA yields were 40% higher than EG at low oxygen mixing ratios (5 hPa). At 180 hPa and 200 hPa [O₂], similar to the concentrations in our study, GA yields were 70% and 95% larger, respectively.

There is no previous estimate for $\alpha_{2.3c}$ or $\alpha_{2.3b}$, both of which would yield glycolaldehyde from the Reaction of RO₂ with HO₂. Shown in Fig. A.5 is the ratio of modeled and measured GA to ethylene glycol as a function of the ratio of HO₂ to RO₂ steady state concentration (as simulated by the box model). Using this comparison of the box model with the data, we find that a branching fraction to the formation of GA of more than 1% from the RO₂ + HO₂ reaction is incompatible with the observations over a wide range of RO₂ fate. This in turn suggests that $\alpha_{2.3c} + 5 \times \alpha_{2.3b}$ is less than 0.01, where the factor of 5 accounts for our determination that in 1 atmosphere of air at 294 K, approximately 20% of alkoxy radicals react via Reaction 2.7b. In our subsequent analysis we assume both $\alpha_{2.3c}$ and $\alpha_{2.3b}$ are zero, producing no GA in our experiments, and attribute excess GA with low partial pressures of O₂ to Reaction 2.4b. We quantify the importance of this reaction pathway by assigning all GA produced in excess of EG in our low [O₂] experiments to this reaction channel. It is also a theoretical possibility that this excess GA is formed by the loss of

a hydrogen atom from alkoxy radicals with excess energy — however, we do not expect such a reaction to be competitive with C-C bond scission or Reaction 2.4b. From our experiments, we determine that the branching to Pathway 2.4b is 26% of the branching to Reaction 2.4c ($\frac{\alpha_{2.4b}}{\alpha_{2.4c}} = .26^{+.05}_{-.26}$). The large uncertainty in this result reflects the fact that this ratio is determined by the difference between the yield of GA and ethylene glycol at 0% O₂ and, as such, is highly sensitive to error in our knowledge of the relative sensitivity of the CIMS to these compounds.

Finally, the extent of Reaction 2.7b to the formation of glycolaldehyde is quantified by comparing the relative concentrations of GA and ethylene glycol at varying O₂ partial pressures. Figure S4 shows $\frac{k_{2.7b}[O_2]}{k_{2.7b}[O_2] + k_{2.7a}}$ as a function of [O₂], which we determine from $\frac{[HOCH_2CHO]}{[HOCH_2CH_2OH]}$ as described in Appendix A.3. This figure also shows this ratio as determined from the data of Barnes et al. (Barnes, Becker, and Ruppert, 1993) and Orlando et al. (Orlando, Tyndall, et al., 1998). Direct comparison of these data is complicated by the difference in total pressure between our experiments and those of Orlando et al. and Barnes et al, which may change the relative branching to decomposition and reaction with O₂. Additionally, the alkoxy radicals in the experiments of Orlando et al. were generated by the reaction of RO₂ with NO. In this system, a temperature-dependent fraction of the alkoxy radicals have excess energy, and undergo prompt decomposition, whereas the rest of the alkoxy radicals are thermalized and can then either undergo decomposition or reaction with O₂ (Orlando, Tyndall, et al., 1998). The fraction of thermalized alkoxy radicals generated in Reaction 2.4 may differ from that generated by the reaction between RO₂ and NO. The analysis of our data, as presented in Appendix A.3, indicates that approximately 20% of the alkoxy radicals in our system react with O₂, whereas 29% of the alkoxy radicals in the system studied by Orlando et al. react with O₂ at 298K. While this difference is well within the uncertainty of our quantification of EG and GA, it may reflect either the difference in pressure or a difference in the fraction of thermalized radicals in our system. The comparison between our data to the data of Orlando et al. and Barnes et al. is discussed further in Appendix A.3. In our subsequent analysis, we use a value of 20% for branching to Reaction 2.7b.

Radical propagation vs chain termination in Reaction 2.4

As described above, in the limit where $F_{external} \rightarrow 0$, Q (Equation 2.11) is a measure of the ratio of the radical propagating channels to the radical terminating channels of Reaction 2.4. In the limit where all HO₂ is produced internally to Reaction 2.4,

> 90% of the HO₂ reacts with HOCH₂CH₂OO, and there are no secondary losses,

$$Q = \frac{[ROOH]}{[HOCH_2CH_2OH] + [ROOR]} \quad (2.11)$$

$$Q_{\text{high RO}_2 \text{ limit}} = \frac{2(\alpha_{R2.4a} + \alpha_{R2.4b})}{\alpha_{R2.4c} + \alpha_{R2.4d}} \quad (2.12)$$

Table 2.3: Quantification of important HOCH₂CH₂OO + HOCH₂CH₂OO reaction parameters and the sources of uncertainty. S_{compound} refers to the sensitivity of the relevant compound. T = 294 K and P = 993 mbar.

Quantity	Constraint	Sources of Uncertainty	Value
$\frac{\alpha_{2.4d}}{\alpha_{2.4c}}$	$\frac{[ROOR]}{[ROH]}$	$\frac{S_{ROOR}}{S_{ROH}}$ (15%) Fit Fig.2.3 (3%) secondary chemistry (3%)	0.57(±.09)
$\alpha_{2.7b}$ (in air)	$\frac{[R=O]}{[ROH]}$	$\frac{S_{R=O}}{S_{ROH}}$ (15%) $\frac{\alpha_{2.4b} + \alpha_{2.4a}}{\alpha_{2.4c}}$ (20%)	0.20(±.1)
$\frac{\alpha_{2.4b}}{\alpha_{2.4c}}$	$\frac{([R=O]_{\text{low } O_2} - [ROH])}{[ROH]}$	$\frac{S_{R=O}}{S_{ROH}}$ (15%)	0.26(+.05) -0.26
$\frac{\alpha_{2.4a} + \alpha_{2.4b}}{\alpha_{2.4c} + \alpha_{2.4d}}$	$\frac{[ROOH]}{[ROH] + [ROOR]}$	Fit Fig. 2.2 (10%) $\frac{S_{ROOH}}{S_{ROH} + S_{ROOR}}$ (15%)	0.54(±.11)
$\alpha_{2.4a}$	$1 - \alpha_{2.4b} - \alpha_{2.4c} - \alpha_{2.4d}$	$\alpha_{2.4b}$ (29%) $\alpha_{2.4c}$ (25%) $\alpha_{2.4d}$ (18%)	0.27(±.10)
$\alpha_{2.4b}$	$\alpha_{3c} \times \frac{\alpha_{2.4b}}{\alpha_{2.4c}}$	$\alpha_{2.4c}$ (25%) $\frac{\alpha_{2.4b}}{\alpha_{2.4c}}$ (15%)	0.10(+.04) -0.10
$\alpha_{2.4c}$	$\alpha_{2.4d} \times \frac{\alpha_{2.4d}}{\alpha_{2.4c}}$	$\alpha_{2.4d}$ (18%) $\frac{\alpha_{2.4d}}{\alpha_{2.4c}}$ (16%)	0.40(±.10)
$\alpha_{2.4d}$	$\frac{[ROOH]}{[ROOR] + [ROH]}$	Fit Fig. 2.4 (10%) $\frac{S_{ROOH}}{S_{ROOR} + S_{ROH}}$ (15%)	0.23(±.05)
$\frac{k_{2.3}^2}{k_{2.13}k_{2.4}}$	$\frac{[ROOH]}{[ROOR] + [ROH]}$	Fit Fig.2.4 (20%) $\frac{S_{ROOH}}{S_{ROOR} + S_{ROH}}$ (15%) F_{external} (15%)	20.2(±6.1)
$k_{2.4}$ ($10^{-12} \frac{\text{cm}^3}{\text{molec s}}$)	$\frac{k_{2.3}^2}{k_{2.13}k_{2.4}}$	$\frac{k_{2.3}^2}{k_{2.13}k_{2.4}}$ (30%) $k_{2.3}$ (30%) $k_{2.13}$ (15%)	2.4(±1.0)

Shown in Figure 2.4 is Q plotted as a function of F_{external} . The y-intercept, ($F_{\text{external}}=0$), is 1.07 suggesting that about half of the RO₂ reacting via R2.4 yields HO₂. The solid line shown in Figure 2.4 is our box model results optimized to fit these data. The model includes external production of HO₂, estimates for the loss of HO₂ via its self reaction, and photolysis losses of both ROOH and the accretion product. The optimized model suggests that the ratio of the radical recycling

channels ($\alpha_{R2.4a} + \alpha_{R2.4b}$) to the radical terminating channels ($\alpha_{R2.4c} + \alpha_{R2.4d}$) is 0.54 ± 0.11 . Independent of the subsequent fate of the alkoxy radical, under our reaction conditions two HO_2 are produced in each of the chain propagating channels. The uncertainty in this ratio represents error in the relative sensitivity of the CIMS to ROOH vs ethylene glycol and ROOR ($\pm 25\%$) and uncertainty in their photolysis frequencies ($\pm 28\%$). As an additional check on the quantification of ROOH, the box model suggests that in the ‘high HO_2 ’ limit, the formation of ROOH should be within a few percent of the reacted ethene. After accounting for the small photolysis losses, we find that the ratio of ROOH to ethene reacted is on average 90% for the high HO_2 experiments (see Figure A.12).

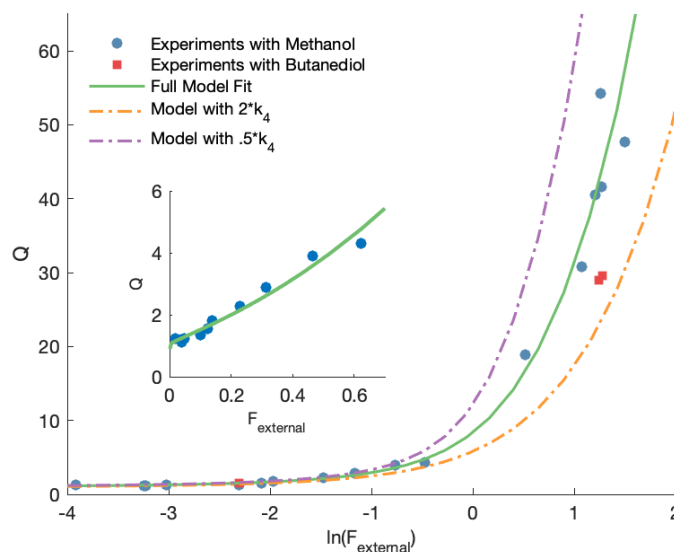


Figure 2.4: Least-squares fit of modelled Q (where $Q = \frac{[\text{ROOH}]}{[\text{HOCH}_2\text{CH}_2\text{OH}] + [\text{ROOR}]}$) to measured Q as a function of $\ln(F_{\text{external}})$. Also shown are the full model run with twice the fitted value of $k_{A.1}$ and half the fitted value of $k_{A.1}$ for comparison. Data points shown in red squares are experiments run with butanediol rather than methanol as an HO_2 source. The inset shows this same fit for lower values of Q as a function of F_{external} .

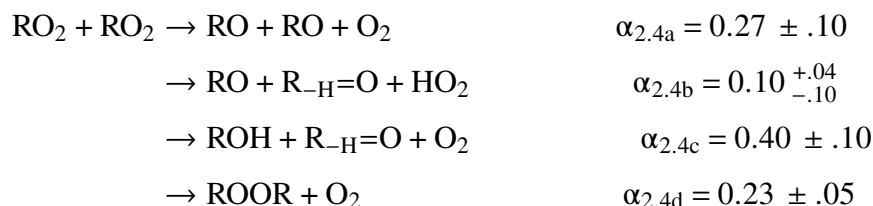
The Rate Coefficient of Reaction A.1

As discussed earlier, when F_{external} is high, Q is proportional to $\frac{1}{2k_{R2.13}} \times \frac{k_{R2.3}^2}{k_{RA.1}(\alpha_{R2.4c} + \alpha_{R2.4d})}$. To estimate $k_{2.4}$ and the branching fractions of Reaction 2.4, we perform a least-squares fit of Q from the box model to Q calculated from our CIMS data. The branching fraction ($\alpha_{2.4d}$) to the formation of the accretion product and the self-reaction rate constant ($k_{2.4}$) are the only fitted parameters. Other unknown param-

eters are written in terms of these parameters using the relationships developed in the previous sections, as demonstrated below:

$$\begin{aligned}\alpha_{2.4c} &= \alpha_{2.4d} \frac{\alpha_{2.4c}}{\alpha_{2.4d}} = 1.72\alpha_{2.4d} \\ \alpha_{2.4b} &= \alpha_{2.4c} \frac{\alpha_{2.4b}}{\alpha_{2.4c}} = .46\alpha_{2.4d} \\ \alpha_{2.4a} &= 1 - \alpha_{2.4b} - \alpha_{2.4c} - \alpha_{2.4d} = 1 - 3.18\alpha_{2.4d}\end{aligned}$$

In addition to constraining $\frac{k_{2.3}^2}{k_{2.13}k_{2.4}}$, we report the value of $k_{2.4}$ assuming the currently accepted value for $k_{2.13}$ (2.5×10^{-12} cm³molecule⁻¹s⁻¹ when accounting for both the termolecular and bimolecular pathways – note that in our experiments, the enhancement due to water vapor and methanol is negligible (Burkholder et al., 2019) and assuming a value of $k_{2.3} = 1.1 \times 10^{-11}$ cm³molecule⁻¹s⁻¹ (Wennberg et al., 2018). Additionally, we report the ratio of the radical propagating channels to the radical terminating channels and the fitted results for all of the branching fractions of the self-reaction pathways (Table 2.3). In summary, we find the following branching fractions for the self-reaction pathways:



Comparison with Earlier Studies

We find the measured branching fraction to formation of the accretion product, $\alpha_{2.4d} = 0.23 \pm .05$, is much larger than that observed by Barnes et al. who found the ROOR formation to contribute at most 1% of the total products. Barnes et al. performed their experiments in a quartz reaction chamber that included metal mirrors. To evaluate the stability of the peroxide accretion product on quartz (and steel), we performed an ethene oxidation experiment in the high RO₂ limit and, during direct sampling into the CIMS, replaced a portion of the Teflon sampling line with a length of approximately 60 cm of quartz or metal tubing, which at our flow rate produced a residence time in the quartz/metal tube of < 3 s. Despite this very short interaction time, we observed a more than a 50% loss of the accretion product (Figure S3). Such wall loss likely limited the ability of Barnes et al. (1993) to observe the ROOR. Additionally, a recent study published on the reactions of ethyl peroxy radicals (Yue et al., 2023) found a branching ratio to the accretion product of

Table 2.4: Comparison between measured kinetic parameters in this and prior studies. We omit from this table the study of Anastasi et al., 1991 as explained in detail in Murrells et al., 1991. Note that $\alpha_{radical}$ is the fraction of the self-reaction that proceeds by radical propagating pathways. Uncertainties on values given in previous studies are the reported uncertainties. ^a $\frac{k_{obs}}{\sigma_{250nm}}$ is the reported value in each study, where applicable, for the observed rate of decay of absorption at 250 nm divided by the cross section at 250 nm. ^b $k_{2.4,recalc}$ is the value of $k_{2.4}$ recalculated given $\alpha_{radical} = .37$ and at 294 K, and $\sigma_{250nm} = 4.75 \times 10^{-18} \text{ cm}^2\text{molec}^{-1}$, as given in Lightfoot et al., 1992. The temperature dependence is taken from Boyd and Lesclaux, 1997. ^cValue taken from Barnes, Becker, and Ruppert, 1993. ^dCalculated at 294 K using the temperature dependence reported in Boyd and Lesclaux, 1997. ^eBoyd et al. used an explicit non-linear fit of the time dependence of the absorption following the flash and it is difficult to directly compare with the results from the Jenkin laboratory. Here, we use the Arrhenius fits provided by Boyd et al. to extrapolate both $k_{2.4}$ and $\alpha_{radical}$ to 294 K. We then multiply the resulting $k_{2.4}$ by $(0.66/(1-\alpha_{radical}(294)))$ to obtain the comparison value.

Study	$\frac{k_{obs}}{\sigma_{250nm}}$ (10^5 cm s^{-1}) ^a	$\alpha_{radical}$	$k_{2.4}$ ($10^{-12} \frac{\text{cm}^3}{\text{molec s}}$)	T (K)	$k_{2.4,recalc}$ ($10^{-12} \frac{\text{cm}^3}{\text{molec s}}$) ^b
This Study		$0.37^{+.10}_{-.15}$	2.4 ± 1.0	294	2.4 ± 1.0
Jenkin and Cox, 1991	6.5 ± 0.4	0.18 ± 0.2	1.4 ± 0.2	298	2.3 ± 0.6
Murrells et al., 1991	6.6 ± 1.1	$0.36 \pm .07$	2.2 ± 0.5	296	2.3 ± 1.3
Jenkin and Hayman, 1995	7.1 ± 0.6	0.50^c	2.1 ± 0.5	298	2.5 ± 1.4
Boyd and Lesclaux, 1997		$0.47 \pm .04^d$	2.4 ± 0.2^d	303	3.0 ± 0.2^e

$10 \pm 5\%$, demonstrating that formation of the accretion product is significant even in small unsubstituted peroxy radical systems, lending further support to our results.

Our estimate of the ratio of radical propagation to radical termination ($\frac{\alpha_{2.4b} + \alpha_{2.4a}}{\alpha_{2.4c} + \alpha_{2.4d}} = 0.54 \pm .11$) in Reaction 2.4 is lower than several recent studies (Barnes, Becker, and Ruppert, 1993; Boyd and Lesclaux, 1997; Jenkin and Hayman, 1995). The study most similar to the work presented here is that of Barnes et al. (Barnes, Becker, and Ruppert, 1993), a product study conducted with FTIR, which reports equal contributions of radical propagating and radical terminating channels. In that work, the concentrations of ethylene glycol, glycolaldehyde, and formaldehyde are compared to determine that $\alpha_{2.4a}$ and $\alpha_{2.4c}$ are approximately equal (Equation 2.18):

$$\frac{\alpha_{2.4c}}{\alpha_{2.4a}} = \frac{[HOCH_2CH_2OH]}{\frac{1}{2}([HOCH_2CHO] - [HOCH_2CH_2OH]) + \frac{1}{4}[HCHO]} \quad (2.18)$$

This expression assumes, however, that additional glycolaldehyde is only formed as a result of alkoxy radical chemistry from Reaction 2.4a and that no accretion product is formed. Barnes et al. did observe excess GA at low O_2 conditions similar to our findings, suggesting an additional source of GA beyond alkoxy chemistry. After

accounting for this channel and the formation of ROOR, our optimized box model is fully consistent with the yields of ethylene glycol, GA, and formaldehyde reported by Barnes et al.

The rate coefficient for the title reaction ($k_{2.4}$) has been measured in several previous studies (Table 2.4). These have all been flash photolysis experiments where the decay of HOCH₂CH₂OO has been monitored by UV spectroscopy. In addition to requiring knowledge of the UV cross sections of this radical, knowledge of the yield and formation timescale of HO₂ is also needed as the reaction of HO₂ with RO₂ contributes significantly to the observed decay rate of RO₂. While the ratio of the decay rate of the RO₂ to the assumed RO₂ cross sections have been similar in these experiments, the reported rate coefficients have varied due to differences in the inferred cross sections and HO₂ chemistry. Most of these studies determine the absolute rate from the observed decay rate of RO₂ by assuming a steady state of HO₂, whereby the following equation holds:

$$k_{2.4,obs} = k_{2.4}(1 + \alpha_{radical}) = k_{2.4}(1 + \alpha_{2.4a} + \alpha_{2.4b}) \quad (2.19)$$

where $\alpha_{radical}$ is the fraction of the self-reaction that proceeds via radical propagating channels. Therefore, the results of these studies are also sensitive to $\alpha_{radical}$. Similar to Boyd and Lesclaux (Boyd and Lesclaux, 1997), using our box model we find that the inferred rate coefficient for Reaction 2.4 from these flash photolysis experiments is somewhat sensitive to assumed kinetics of the HO₂ chemistry and the details of how the absorption data are fitted (fitting window and signal-to-noise). Nevertheless, to place these different studies on a similar footing, we use the reported decay rate of the UV absorption at 250nm and a common value for the UV cross section of the peroxy radical (assumed to be $4.75 \times 10^{-18} \text{ cm}^2 \text{ molec}^{-1}$) (Lightfoot et al., 1992) and use Equation 2.19 with the recycling fraction from this work. Finally, we adjust for the difference in the experimental temperature using the temperature dependence for Reaction 2.4 from Boyd and Lesclaux (Boyd and Lesclaux, 1997). These are reported in the last column of Table 2.4.

The experiments reported here provide an entirely different constraint on the kinetics. Here, we quantify the relative reaction rate of the RO₂ with itself vs with HO₂ under conditions where the ratio of the production rates of HO₂ to RO₂ is known, and obtain a value of $k_{2.4} (294\text{K}) = 2.4 \pm 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Despite the very different approaches and entirely different error sources, our inferred rate coefficient for Reaction 2.4 is remarkably similar to the kinetics measurements by flash photolysis.

2.4 Conclusions

Bimolecular peroxy radical reactions play an important role in the chemistry of the troposphere, and accurately measuring the rates of these reactions relative to other important RO_2 loss processes is central to determining their ultimate effect on air quality. In this study, we have shown that the accretion product formed in the reaction of the ethene-derived peroxy radical is likely a peroxide and is produced with a branching fraction of approximately 23%. We have further measured the ratio of radical propagating to radical terminating chemistry as well as the branching to glycolaldehyde, which is produced in both chain propagating and chain terminating channels. Finally, we have constrained the rate coefficient of the title reaction relative to the reaction rate coefficient of the peroxy radical with HO_2 , and obtain a value consistent with those of previous flash photolysis studies. The branching fractions and kinetics along with their uncertainties (derived from comparison of our observations with a box model) are summarized in Table 2.3. Future studies will extend the methods discussed here to study the $\text{RO}_2 + \text{RO}_2$ chemistry in more diverse systems.

Chapter 3

ACCRETION PRODUCT FORMATION IN THE SELF- AND CROSS-REACTIONS OF SMALL ALKENE-DERIVED PEROXY RADICALS

3.1 Introduction

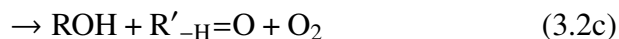
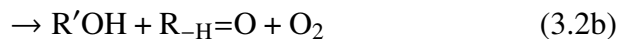
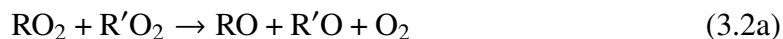
The oxidation of anthropogenic and biogenic hydrocarbons is one of the primary drivers of tropospheric chemical processes. Upon emission to the atmosphere, these hydrocarbons are primarily oxidized by OH, O₃, or NO₃, followed by addition of O₂ to form peroxy radicals (RO₂) (Atkinson, 1997b). The radical cycling and ultimate fate of these RO₂ has significant implications for, among other important processes, the formation of ozone and particulate matter (Lightfoot et al., 1992; Jenkin and Clemitshaw, 2000; Tyndall et al., 2001). In polluted areas such as urban centers, where nitrogen oxides (NO_x = NO + NO₂) tend to be high, RO₂ primarily react with NO (Jenkin and Hayman, 1995; Boyd, Lesclaux, et al., 1996). This reaction leads either to a radical recycling channel, in which NO₂ and an alkoxy radical (RO) are formed, or to the formation of an organic nitrate (RONO₂) (Orlando and Tyndall, 2012; Seinfeld and Pandis, 2016). The former propagates the radical cycle that leads to ozone formation, while the latter can lead to the formation of secondary organic aerosol (SOA) or transport of NO_x to regions removed from the original source (Perring, Pusede, and Cohen, 2013).

In regions where NO_x is low, RO₂ will undergo unimolecular reaction (Crounse, Nielsen, et al., 2013) or bimolecular reactions with (primarily) HO₂ or other RO₂ (Orlando and Tyndall, 2012; Jenkin, Valorso, et al., 2019). This chemistry is important in remote regions and is even becoming important in urban areas as NO_x continues to decrease due to emission regulations (US EPA, 2014; Winkler et al., 2018). The reaction of RO₂ with HO₂ can, similarly to the reaction with NO, lead to radical propagation (Reaction 3.1b and 3.1c) or radical termination (Reaction 3.1a) via the formation of a hydroperoxide (ROOH) (Orlando and Tyndall, 2012).



While Reaction 3.1a is the dominant pathway for most alkyl peroxy radicals, Reactions 3.1c and 3.1b have been observed to play an important role in the reactions of oxygenated peroxy radicals, including β -hydroxy peroxy radicals, with HO_2 (Jenkin, Valorso, et al., 2019). Although the reaction rates of peroxy radicals with HO_2 and the branching to products remains uncertain for many peroxy radicals, structure activity relationships suggest that the rate coefficient of the $\text{RO}_2 + \text{HO}_2$ reaction largely depends on the number of heavy atoms in the peroxy radical and exhibits little dependence on substitution or structure (Wennberg et al., 2018).

The reaction of RO_2 with $\text{R}'\text{O}_2$ (the so-called ‘permutation’ or cross-reaction, Reaction 3.2) or with itself (the self-reaction, $\text{R} = \text{R}'$) proceeds primarily via three reaction pathways: the formation of two alkoxy radicals (Reaction 3.2a), the formation of an alcohol and a carbonyl (Reaction 3.2c and 3.2b), or the formation of a peroxide accretion product (Reaction 3.2d) (Jenkin, Valorso, et al., 2019; Orlando and Tyndall, 2012).



Generally, when $\text{R} = \text{R}'$, the rate of Reaction 3.2 decreases as the substitution of the peroxy radical increases, and increases with the addition of a hydroxy or acyl substituent (Jenkin, Valorso, et al., 2019). Although this trend has been observed for self-reactions, the relationship between the kinetics of cross-reactions ($\text{R} \neq \text{R}'$) and self-reaction rates of the constituent peroxy radicals (RO_2 and $\text{R}'\text{O}_2$) remains poorly characterized.

The branching to the various products of Reaction 3.2 remains uncertain and has been the focus of substantial recent research. Most notably, it was previously widely accepted that Reaction 3.2d was negligible, as the resulting accretion products were not observed in laboratory oxidation studies and the proposed formation mechanism, involving an intersystem crossing, appeared unfavorable (Orlando and Tyndall, 2012; R. Lee et al., 2016; Valiev et al., 2019). However, several recent studies have reported the formation of dimers in various oxidation systems. While some of these dimers are esters formed in the particle-phase (Kenseth et al., 2018) or via other gas-phase accretion mechanisms (Peräkylä et al., 2023), several of these products observed with chemical ionization mass spectrometry (CIMS) have masses consistent with

the formation of the ROOR and are reported to form at appreciable rates that even approach the collision rate (Berndt, Mentler, et al., 2018; Molteni et al., 2019; Kwan et al., 2012; Berndt, Richters, Kaethner, et al., 2015). The formation of the ROOR is atmospherically significant both because it terminates the radical cycle (at least temporarily) and because these products have low volatilities and are likely to play a role in the formation of secondary organic aerosol (SOA). In fact, these compounds have been observed in the remote ambient environment in both the gas- and the particle-phase, demonstrating the role that these dimers play in particle formation (B. H. Lee, Lopez-Hilfiker, et al., 2018). Additionally, a possible fourth pathway for Reaction 3.2 leading to an alkoxy radical, carbonyl, and HO₂ was proposed for the self-reaction of the hydroxy ethyl peroxy radical (Murphy et al., 2023), further highlighting the need for additional study of the self-reaction for a variety of peroxy radical precursors.

Recently, accretion product formation has been reported for the self-reactions of ethyl peroxy (Yue et al., 2023), hydroxy ethyl peroxy (Murphy et al., 2023), and propyl peroxy radicals (Liu et al., 2024), with branching fractions of 10(±5)%, 23(±5)%, and 10(±5)% respectively. In each of these studies, the identity of the dimers was confirmed to be the ROOR formed in Reaction 3.2d by either gas chromatography or vacuum ultraviolet (VUV) photoionization mass spectrometry.

Despite these recent insights into the formation of accretion products via peroxy radical self- and cross-reactions, these studies have only been conducted for a limited number of peroxy radical precursors. There have been no studies that have systematically examined the relationship between the rate of accretion product formation and peroxy radical structure. However, it is necessary to probe this relationship to predict the formation rate of the accretion product for the wide variety of peroxy radicals present in the atmosphere.

In this study, we begin to fill this gap by expanding on the work presented in Chapter 2 on the formation of the accretion product in ethene-derived hydroxy peroxy radical systems. Specifically, we show that the accretion product forms in a variety of small-alkene-derived peroxy radical systems and measure the formation rate of the accretion product in each of these oxidation systems relative to the formation rate of the ethene-derived accretion product. By measuring this rate in the propene, methylpropene, and cis-2-butene oxidation systems, we examine the relationship between accretion product formation and structure for these small alkene systems. Using literature values for these rate constants where available, we further estimate

the branching to the accretion product in each of these systems.

3.2 Methods

Experimental Design

In this study our goal is to quantify the formation of the peroxide accretion product for a series of small alkene-derived peroxy radicals. In each case, the peroxy radicals of interest are formed by the addition of OH to the parent alkene, followed by the rapid addition of O₂ to form the peroxy radical:



In all of our experiments, OH was generated by the photolysis of H₂O₂ (Reaction 3.4) via the illumination of eight Sankyo Denki G40T10 254 nm lamps for an average of 2 minutes. The photolysis rate of H₂O₂ under these conditions in our 800 liter FEP Teflon environmental chamber has been previously measured to be $3.0(\pm 0.5) \times 10^{-4} \text{ s}^{-1}$ (Murphy et al., 2023).



In several of the experiments reported here, the fraction of alkene reacted over the photolysis period was estimated by simultaneously observing the formation of glycolaldehyde in the reaction of ethylene glycol with OH (Reaction 3.5).



The currently recommended value for the reaction of ethylene glycol with OH is $1.45 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($\Delta \log k = \pm 0.20$) (Atkinson et al., 2006). In experiments where ethylene glycol was used as a probe of the OH exposure, approximately 20-70 ppb of ethylene glycol was injected. The OH exposure was then calculated using the measured production rate of glycolaldehyde from a known concentration of ethylene glycol. This calculation yielded estimated OH exposures ranging between 0.4×10^9 - $6.0 \times 10^9 \text{ molecules cm}^{-3} \text{ s}$ across the various alkene systems and conditions used here. In these systems, the OH exposure was also calculated using our photochemical box model, and values agree within a factor of 2. Therefore, in experiments in which no OH probe was used, the photochemical box model was used to estimate the fraction of reacted alkene.

We performed a suite of experiments to quantify the product of the self-/cross-reaction rate coefficient ($k_{3,2}$) times the branching fraction leading to accretion

products ($\alpha_{3,2d}$) of many $RO_2 + RO_2$ reactions relative to the value measured for ethene in our previous work ($k_{3,2}\alpha_{3,2d} = 5.5(\pm 2.6) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Murphy et al., 2023). We oxidized mixtures of ethene with either propene, 2-methylpropene, or cis-2-butene and observed the formation of accretion products from all combinations of the resulting $RO_2 + RO_2$ reactions. To estimate $k_{3,2}\alpha_{3,2d}$, experiments were performed under conditions where most ($> 88\%$) of the peroxy radicals react with HO_2 via Reaction 3.1a to form $ROOH$. Under these conditions, the ratios of the observed concentrations of $ROOH$ provide a constraint on the ratios of the parent RO_2 concentrations (Equation 3.6):

$$\frac{[RO_2]_{HC}}{[RO_2]_E} = \frac{[ROOH]_{HC} k_{3,1,E} \alpha_{3,1a,E}}{[ROOH]_E k_{3,1,HC} \alpha_{3,1a,HC}} \quad (3.6)$$

where HC = non-ethene hydrocarbon, E = ethene, $k_{3,1,E}$ and $k_{3,1,HC}$, are the rate coefficients of Reaction 3.1 for ethene and non-ethene hydrocarbons, respectively, and $\alpha_{3,1a,E}$ and $\alpha_{3,1a,HC}$ are the branching fractions to $ROOH$. According to our photochemical box model, Equation 3.6 is accurate to within 20% under the conditions of our experiments.

To ensure that the $[HO_2]/[RO_2]$ ratio satisfies this condition, we add sufficient concentrations of methanol such that the reaction of OH with methanol exceeds the reaction of OH with the alkenes, as has been described previously (Murphy et al., 2023). In the oxidation experiments performed in this study, the relative concentrations of methanol and parent hydrocarbon yielded steady state $[HO_2]/[RO_2]$ ratios above 2.0 (as estimated by our box model). Because the rate coefficients for the reaction of RO_2 with HO_2 ($k_{3,1}$) are more than an order of magnitude faster than the rate coefficients of the self- and cross-reactions ($k_{3,2}$) for the systems studied here, the requirement that the peroxy radicals react overwhelmingly with HO_2 is satisfied under these conditions.

The $k_{3,2}\alpha_{3,2d}$ for each alkene can then be obtained from the measured ratio of the accretion product of interest to the ethene-derived accretion product. For a given isomer of a peroxy radical derived from a non-ethene hydrocarbon (in this case propene, methylpropene, or cis-2-butene), the $k_{3,2,HC}\alpha_{3,2d,HC}$ value is given by Equation 3.7, where the ratio of the RO_2 concentrations is obtained from Equation 3.6:

$$k_{3,2,HC}\alpha_{3,2d,HC} = k_{3,2,E}\alpha_{3,2d,E} \left(\frac{[RO_2]_E}{[RO_2]_{HC}} \right)^2 \left(\frac{[ROOR]_{HC}}{[ROOR]_E} \right) \quad (3.7)$$

If the accretion product of interest is formed via the cross-reaction of two isomers of the same non-ethene hydrocarbon (HC_a and HC_b), this equation becomes:

$$k_{3,2,HC_a,b} \alpha_{3,2d,HC_a,b} = k_{3,2,E} \alpha_{3,2d,E} \left(\frac{[RO_2]_E}{[RO_2]_{HC_a}} \right) \left(\frac{[RO_2]_E}{[RO_2]_{HC_b}} \right) \left(\frac{[ROOR]_{HC_a,b}}{[ROOR]_E} \right) \quad (3.8)$$

Finally, for determination of the $k_{3,2} \alpha_{3,2d}$ value for the cross-reaction between an isomer of a non-ethene hydrocarbon and ethene, Equation 3.7 reduces to:

$$k_{3,2,HC+E} \alpha_{3,2d,HC+E} = k_{3,2,E} \alpha_{3,2d,E} \left(\frac{[RO_2]_E}{[RO_2]_{HC}} \right) \left(\frac{[ROOR]_{HC+E}}{[ROOR]_E} \right) \quad (3.9)$$

Using Equations 3.7-3.9, we calculate the $k_{3,2} \alpha_{3,2d}$ values for all of the self- and cross-reactions of the peroxy radical systems studied here.

Our estimate of $k_{3,2} \alpha_{3,2d}$ is particularly sensitive to $k_{3,1}$ and $\alpha_{3,1a}$. $k_{3,1}$ is estimated here using the structure activity relationship (SAR) found in Wennberg et al. (2018). This rate constant has been measured for the primary peroxy radical derived via the oxidation of 2-methylpropene ($k_{3,1} = 1.5(\pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Boyd, Lesclaux, et al., 1996) and the secondary peroxy radical derived via the oxidation of cis-2-butene ($k_{3,1} = 1.5(\pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Jenkin and Hayman, 1995). These measured values are the same as those values predicted by the structure-activity relationship within error ($1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K for both compounds), and so the SAR values are used in all cases for consistency.

Estimates of $\alpha_{3,1a}$ were derived from the concentration of ROOH formed in the high HO_2 experiments. In these experiments, the amount of ROOH formed divided by the concentration of the reacted alkene is equal to the branching fraction to Reaction 3.1a (Equation 3.10).

$$\frac{\Delta[ROOH]}{\Delta[HC]} = \alpha_{3,1a,HC} \quad (3.10)$$

According our photochemical box model, for the conditions of our experiments, Equation 3.10 is accurate to better than 9%. There is additional error induced by the estimation of the reacted alkene used in the calculation of $\alpha_{3,1a}$. In experiments where ethylene glycol was included as a probe of OH exposure, we found that the modelled and measured OH exposure agreed to within a factor of 2. Therefore, we assign the modelled OH exposures, and by extension the fraction of reacted

alkene, an uncertainty of 50%. This is by far the largest source of uncertainty in the estimation of $\alpha_{3.1a}$. Further, this error is much larger than that induced by the uncertainties in the values of $k_{3.1}$. Therefore, we assign the $\alpha_{3.1a}$ an uncertainty of 50% and the overall calculation of $k_{3.2}\alpha_{3.2d}$ a corresponding uncertainty of 50%.

Finally, to assist in assigning the different ROOR isomers in the gas chromatograms, we performed experiments where we did not add methanol in order to maximize the fraction of RO_2 undergoing self- and cross-reactions and thus the signal-to-noise ratios of the resulting chromatograms. These experiments are labeled ‘high RO_2 ’ in the discussion below and generally contained $[\text{HO}_2]/[\text{RO}_2]$ ratios that were much less than 1.

Instrumentation

All measurements in this study were conducted using the Caltech gas chromatograph chemical ionization mass spectrometer (GC-CIMS). This instrument has been described in detail previously (Vasquez, Allen, et al., 2018), but a brief description is given here.

The Caltech high-resolution time-of-flight chemical ionization mass spectrometer (HRTof-CIMS) uses CF_3O^- as a reagent ion, which is produced via the interaction of dilute CF_3OOCF_3 gas in N_2 with polonium-210. In direct sampling mode, the analyte gas is sampled at approximately 2000 sccm, and 180 sccm of this sample passes through a Teflon-coated metal frit into a Teflon-coated glass flow tube that is maintained at a pressure of approximately 35 mbar. Here, the sample is diluted with N_2 and turbulently mixes with the 380 sccm flow from the ion source. The analytes are then ionized by reaction with the reagent ion. For most of the compounds considered here, the analyte forms a cluster with the reagent ion that appears at a mass-to-charge ratio of the molecular weight of the compound plus the mass of CF_3O^- ($m/z = \text{mw} + 85$). However, analytes may also undergo a fluorine transfer reaction, thus appearing at a mass-to-charge ratio equal to the molecular weight of the analyte plus the mass of fluorine ($m/z = \text{mw} + 19$). Although fragmentation in this ionization scheme is minimal compared to the fragmentation observed in other chemical ionization schemes, some compounds still lead to characteristic fragments. For example, organic hydroperoxides characteristically form fragment ions at m/z 63 and m/z 81 (Paulot, Crounse, et al., 2009; St. Clair et al., 2014; Crounse, Paulot, et al., 2011). The ionized analytes are then directed into the mass spectrometer through a pinhole and a conical hexapole ion guide, where they are subsequently

detected. Signals were collected for mass-to-charge ratios between m/z 19 and m/z 396, and the mass resolving power of the instrument is approximately 3000 $m/\Delta m$.

The metal-free, low-pressure gas chromatograph consists of a 2-meter silica-coated column that is cooled via the expansion of liquid CO_2 and heated with resistance heaters. In these experiments, the analyte gas was sampled at approximately 1200 sccm and diluted via the addition of a nitrogen flow perpendicular to the sample flow. The diluted sample was then collected in a small trap prior to the column at -10°C , -20°C , or -30°C for approximately 2-10 min, with the chosen trapping temperatures, dilution factors, and trapping times chosen to maximize the concentration of analyte trapped while avoiding the trapping of water. After trapping, the temperature was increased to 130°C at a pre-determined ramping rate. The effluent is then directed into the flow tube with a 200 sccm pickup flow of nitrogen and detected by the HRTof-CIMS. The HRTof-CIMS can readily be switched to sample from the GC or directly from the chamber. A complete list of the temperature ramps and trapping conditions used in these experiments is given in Appendix B.1.

CIMS Calibration and GC Collection and Transmission Efficiencies

The sensitivity of the CIMS to most compounds in this study was estimated using the sensitivities of chemically similar compounds. In prior work, we measured a sensitivity of $2.5(\pm 0.2) \times 10^{-4}$ cts/pptv of the CIMS to ethylene glycol (Murphy et al., 2023). The sensitivities of the other RO_2 reaction products were then estimated via calculation of their ion-molecule collision rates relative to that of ethylene glycol. This procedure is described in detail in previous work (Murphy et al., 2023), but is briefly summarized here. The CIMS instrument used in this work implements a transverse ionization scheme that results in a short interaction time (approximately 5 ms) between the analyte and reagent ions. In this implementation, the sensitivity of the analyte is approximately proportional to the ion-molecule collision rate, the fraction of these collisions that result in ionization of the analyte, the transmission efficiency of the resulting ions, and any fragmentation of the analyte in the ionization process. Further, this sensitivity also depends on the total number of reagent ions (which includes CF_3O^- and its clusters with water and H_2O_2) - since the fraction of reagent ions reacting with analytes is low, we can normalize the analyte signals to the total reagent ion signal. Specifically, to remain in a linear counting regime, we normalize our signals to the sum of the signals of the isotopic analogues of the reagent ions ($m/z = 86, 104, \text{ and } 120$). The resulting signals are then proportional to the concentration of the analyte in the sample.

CF_3O^- binds particularly strongly to multifunctional organic compounds (Hyttinen et al., 2018), and so the fraction of the analyte that undergoes ionization generally depends on the ion-molecule collision rate. For analytes that form weakly bound clusters (such as H_2O_2), not every collision results in the formation of a stable ion cluster. Such analytes are generally identified by probing the relationship between the sensitivity and the temperature and humidity, as the sensitivity of these compounds tends to exhibit a negative dependence on temperature and a complex dependence on water concentration (Crounse, McKinney, et al., 2006). The efficiency of cluster formation following collision may also decrease due to fragmentation of the analyte. In our previous work on the ethene-derived peroxy radical self-reaction, we found that the clusters of the resulting RO_2 products with the reagent ion were well bound and exhibited little fragmentation. Due to the similar sizes and chemical structures of the compounds studied here compared to those probed in the prior study, we assume that the compounds considered in this study are similarly well-bound and thus that their sensitivities will scale with their ion-molecule collision rates. The sensitivities of the compounds measured in this study are then estimated by calculating their ion-molecule collision rates relative to ethylene glycol and using this scaling factor to obtain the sensitivity from the measured ethylene glycol sensitivity. The calculated ion-molecule collision rates relative to ethylene glycol are given in Appendix B.2 and are obtained using the methods outlined in Su et al. (1982) and quantum calculations of the dipole moments and polarizabilities of the relevant compounds (Garden et al., 2009). Where quantum calculations of polarizabilities and dipole moments were not available, the sensitivity of the compound was assumed to be the same as the most chemically similar compound for which the ion-molecule collision rate was available.

The GC collection and transmission efficiencies for each compound were determined by comparison of the sum of the total GC signal to the average CIMS signal. The collection and transmission efficiencies ranged between 10% and 100% – the lowest values generally reflect small ketones and alcohols for which the trapping was inefficient. The average transmissions of each of the relevant compounds is given in Appendix B.3.

Isomer Distribution

The calculations of the self- and cross-reaction rate constants for the individual isomers of the various peroxy radicals required the separation of the various isomers of the resulting RO_2 products in the gas chromatograph and the subsequent

quantification of their concentrations. The relative concentrations of each of these isomers was determined by fitting each peak using a modified open-source MATLAB peak-fitting function (O'Haver, 2017). These GC peaks are best fit in our instrument to an exponentially-broadened Gaussian with varying peak widths and exponential time constants. The peak widths and time constants that minimized the total error for these fits were determined by performing a bootstrap best-fit procedure in which 1,000-10,000 trials were performed with the parameters randomly varied in a range equal to $\pm 50\%$ of the initial guess. The resulting best-fit parameters, which are provided in Appendix B.4 for the experiments discussed here along with the errors and R^2 values of the fits, were then used to calculate the area under each chromatographic peak.

To account for transmissions and trapping efficiencies less than unity in the GC, we did not calculate the concentration of each isomer directly from this integrated GC signal. Rather, the relative proportion of each compound was calculated using the ratio between the calculated areas and these proportions were subsequently multiplied by the total signal in the CIMS to determine the concentrations of each isomer. In this calculation, we implicitly assume that the direct sampling signal represents the total concentration of a given set of isobaric isomers and that the trapping and transmission efficiencies of these different isomers are the same.

Reagent Preparation

H₂O₂ (30% by mass, Macron Fine Chemicals) was measured by weight into a pre-weighed three-way glass vial and injected into the chamber by evaporating this weighed sample with dry air flowing at 20 SLM. The glass vial was reweighed following injection to ensure complete evaporation of the sample. Ethylene glycol (Sigma-Aldrich) was injected in a similar manner, with the glass vial partially immersed in warm water to ensure evaporation of the sample.

Ethene ($\geq 99.5\%$, Sigma-Aldrich), methanol ($\geq 99.9\%$, Sigma-Aldrich), 2-methylpropene (99%, Sigma Aldrich), cis-2-butene ($\geq 99\%$, Sigma Aldrich), and propene ($\geq 99\%$, Sigma Aldrich) samples were measured into 500-mL glass bulbs via a manometric system in which the bulb is attached simultaneously to a vacuum/N₂ system and to the reagent source. The desired concentration of the relevant hydrocarbon was then obtained by serial dilution with pressure measurements conducted using pressure sensors (MKS 1000 and 10 Torr baratron pressure transducers). The purity of the samples and the concentrations measured using manometry were confirmed by tak-

ing IR spectra in a 19 cm pyrex FTIR cell with CaF₂ windows and fitting the resulting spectra to cross sections obtained from the PNNL IR Database (Sharpe, Sams, and Johnson, 2002). The measurements taken with manometry and the concentration calculated from the FTIR spectra agree to within 30%.

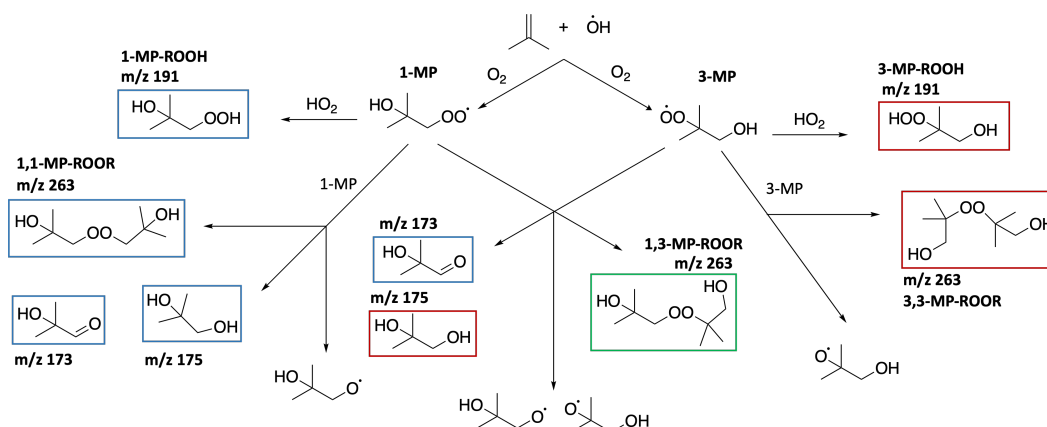
3.3 Results and Discussion

2-Methylpropene

The expected products of the NO_x-free OH-initiated oxidation of 2-methylpropene are shown in Scheme 3.1. Two peroxy radical isomers, a tertiary peroxy radical (3-MP) and a primary peroxy radical (1-MP), are formed via the major and minor OH addition reactions, respectively. Hydrogen abstraction has been found to account for <5% of the overall reaction of 2-methylpropene with OH and is therefore neglected in this analysis (Atkinson, 1997b; Teng, Crounse, L. Lee, et al., 2015). Representative chromatograms of the major accretion and hydroperoxide products are given in Figure 3.1.

In experiments with high HO₂/RO₂ ratios ($\frac{HO_2}{RO_2} > 2$), the isomeric distribution of the ROOH products is expected to reflect the ratio of the production rates of the peroxy radical isomers, due to the observed lack of dependence of $k_{3,1}$ on peroxy radical structure (Wennberg et al., 2018). In these high HO₂ experiments, the average distribution of 1-MP-ROOH/3-MP-ROOH is 16(±1)%/84(±1)%. This is within 5% of the isomer distribution found by Teng et al. (21(±2)%/79(±2%)) (Teng, Crounse, L. Lee, et al., 2015), further confirming that the primary loss of RO₂ in these experiments is reaction with HO₂.

In the high RO₂ regime ($\frac{HO_2}{RO_2} \ll 1$), the fraction of 1-MP-ROOH is significantly lower than that observed in the high HO₂ condition, with an average isomer distribution of 3(±1)% 1-MP-ROOH and 97(±1)% 3-MP-ROOH. Under these conditions, the ROOH isomer distribution is significantly altered by the loss rates of 3-MP and 1-MP RO₂ due to self- and cross-reaction chemistry. The dramatic decrease in the production of 1-MP-ROOH relative to 3-MP-ROOH is consistent with previous observations that the rate of self- and cross-reactions of primary peroxy radicals are rapid compared to those of tertiary peroxy radicals (Jenkin, Valorso, et al., 2019).



Scheme 3.1: Reaction scheme for the oxidation of 2-methylpropene by OH. Stable products that can be observed with the CF₃O⁻ GC-CIMS are boxed and color-coded such that products that are derived from the primary peroxy radical are in blue, those derived from the tertiary peroxy radical are in red, and products formed from the cross-reactions of the primary and tertiary peroxy radicals are in green. Each product is labelled with the m/z of that product in our CIMS, which is equal to the molecular weight + 85. In the presence of O₂, the alkoxy radicals shown will decompose to formaldehyde and acetone.

The isomer distribution of the methylpropene-derived accretion product formed in Reaction 3.2 is influenced by the competing factors of peroxy radical abundance and reaction rate. Although the branching to the formation of tertiary peroxy radicals in the OH-initiated oxidation of 2-methylpropene is approximately 80% (Teng, Crounse, L. Lee, et al., 2015), the self-reactions of tertiary peroxy radicals are generally several orders of magnitude slower than those of primary peroxy radicals (Orlando and Tyndall, 2012; Jenkin, Valorso, et al., 2019). In the high RO₂ condition three isomers at the mass of the accretion product (m/z 263) are observed, consistent with the expected products outlined in Scheme 3.1. Therefore, we see that the accretion product is formed at appreciable rates in all three of the possible self- and cross-reactions observed in this oxidation system.

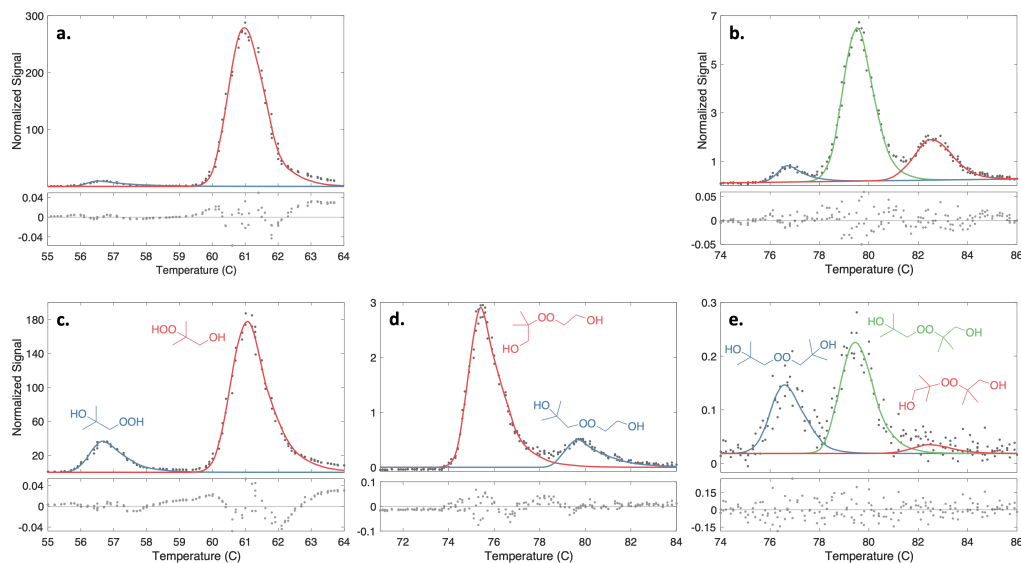


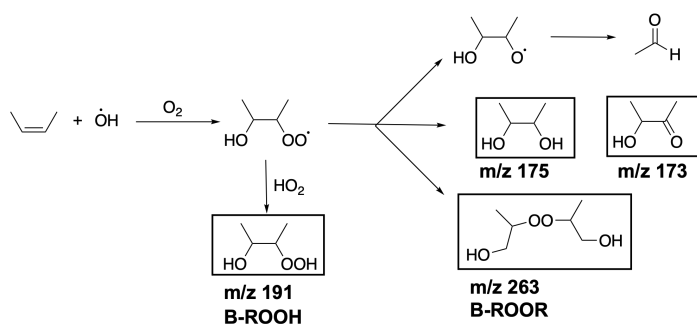
Figure 3.1: Representative chromatograms of ROOH (a. and c.) and ROOR (b., d., and e.) products formed in the high RO₂ (upper panel) and high HO₂ (lower panel) oxidation of 2-methylpropene. Experiments represented in the lower panel also included ethene. The experimentally measured signal is given as dark gray dots, while the colored lines are the bootstrap best fits of the chromatographic data. The corresponding structures are the suggested assignments of these peaks. Below each chromatogram are plots of the residuals of the best fits given as fractions of the maximum peak value.

The peak assignments given in Figure 3.1 follow the observation that, in the Caltech GC-CIMS instrument, compounds with primary -OH groups elute at higher temperatures than those with tertiary -OH groups due to the corresponding decrease in interaction between the analyte and the column (Xu, Møller, Crounse, Otkjær, et al., 2019). The ROOR produced in the cross-reaction of 1-MP and 3-MP (1,3-MP-ROOR) is produced in the highest proportion, constituting on average 69(±4)% of the total concentration of methylpropene-derived accretion products. That formed in the self-reaction of 3-MP (3,3-MP-ROOR) constitutes 23(±3)% of this signal, with 7(±2)% of the signal on average attributed to the peroxide formed in the self-reaction of 1-MP (1,1-MP-ROOR). Clearly, the cross-reaction between 1-MP and 3-MP is favored over the self-reaction of 3-MP. However, the 1-MP reacts quickly such that the steady state concentration of 1-MP is quite low and a significant concentration of 3,3-MP-ROOR is formed despite the slow self-reaction rate constant of tertiary peroxy radicals. These observations are further quantified and discussed in the section on ROOR formation rates below.

In experiments with high HO_2/RO_2 ratios, 2-methylpropene and ethene were oxidized together to measure the relative production rates of the ethene- and methylpropene-derived accretion products, as described in the Methods section. Under these conditions, the proportion of 3,3-MP-ROOR decreases appreciably to between 0-5% of the total methylpropene-derived ROOR concentration. The signal-to-noise ratio of this peak is very low, with the peak indistinguishable from the noise in some cases - therefore, significant uncertainty is assigned to this fitted peak area. On the other hand, the concentrations of 1,1-MP-ROOR and 1,3-MP-ROOR are comparable, with average proportions of $37(\pm 1)\%$ and $61(\pm 2)\%$, respectively. Further, two compounds are observed at m/z 235, consistent with accretion products formed in the cross-reactions of 2-methylpropene and ethene-derived peroxy radicals (E-1-MP-ROOR and E-3-MP-ROOR). These compounds are produced in unequal proportions, with a distribution of $78(\pm 3)\%/22(\pm 3)\%$. The observed decrease in the concentrations of 3,3-MP-ROOR and 3,1-MP-ROOR relative to 1,1-MP-ROOR in the presence of ethene suggests that 3-MP preferentially reacts with ethene-derived peroxy radicals over reaction with 1-MP or 3-MP. We thus assign the more prominent peak at m/z 235 to E-3-MP-ROOR. Once again, these observations will be discussed and quantified further in the section on ROOR formation rates.

Cis-2-Butene

The simplified mechanism of the NO_x -free OH-initiated oxidation of cis-2-butene is given in Scheme 3.2. Once again, stable products that can be observed via clustering with CF_3O^- in the Caltech GC-CIMS are boxed and labelled with the corresponding m/z . The H-abstraction pathway is once again expected to be negligible ($<5\%$ of the total reaction with OH). In contrast to the 2-methylpropene system, the symmetry of the parent molecule yields only one possible structural isomer of the peroxy radical. However, three stereoisomers of the peroxy radical (two enantiomers and a meso compound) are possible, and these will react to form distinct ROOH, ROOR, and diol products that have the potential to be chromatographically separated (for simplicity, stereoisomers are not shown in Scheme 3.2). Representative chromatograms of the resulting peroxide, hydroperoxide, and diol products are given in Figure 3.2.



Scheme 3.2: Reaction scheme for the oxidation of cis-2-butene by OH in the presence of O₂. Stable products that can be observed with the CF₃O⁻ GC-CIMS are boxed and labelled with the m/z at which they are observed. For simplicity, stereoisomers are not included.

As described above, three stereoisomers of the peroxy radical are generated, the reactions of which are expected to produce multiple stereoisomers of the resulting B-ROOH, B-ROOR, and 2,3-butanediol products. In agreement with this expectation, two closely separated peaks are observed in the chromatogram at m/z 175, the mass-to-charge ratio at which 2,3-butanediol appears in the CIMS, with a distribution of 37(±8)%/63(±8)% in the high RO₂ ($\frac{[HO_2]}{[RO_2]} \ll 1$) experiments. Comparison of this chromatogram with that of a 2,3-butanediol standard containing a mixture of stereoisomers confirms the identity of these peaks as the stereoisomers of 2,3-butanediol (see Fig. B.1). Due to the chemical similarity of the enantiomers, we hypothesize that one of these peaks is a mixture of the enantiomers, while the other is the meso compound. However, we cannot definitively assign these peaks at this time. In contrast, multiple peaks are not observed at the masses associated with the ROOH and ROOR products, likely due to a lack of chromatographic separation.

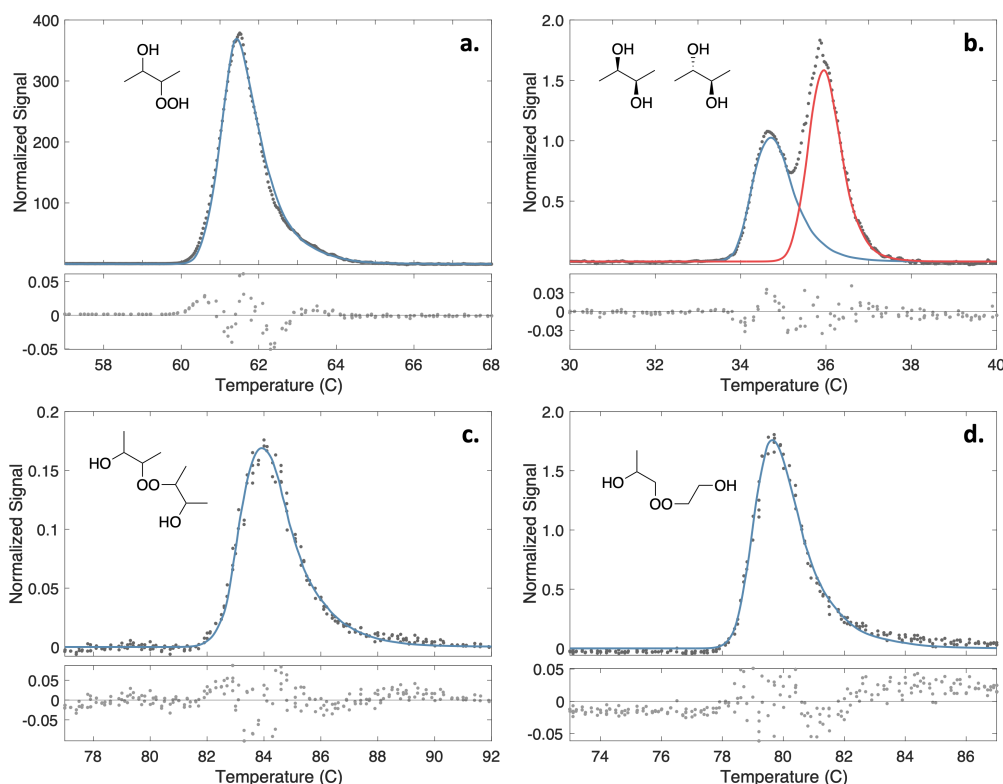


Figure 3.2: Sample gas chromatograms of several important masses produced in the oxidation of cis-2-butene by OH in the presence of O₂ and ethene, including (a) the ROOH, (b) the diol, (c) the ROOR formed in the self-reaction, and (d) the ROOR formed in the cross-reaction with ethene. Experimentally measured signals are given in gray dots, while the bootstrapped best fits to these peaks are given in colored lines. The provided structures correspond to the assignments of these peaks - the two structures in b. are not assigned to a particular peak. Below each chromatogram the residuals of the best fits are plotted as a fraction of the maximum peak signal. The chromatograms in a. and b. are corrected for significant tailing - this correction is described in Appendix B.5.

There is a significant tailing observed in the chromatogram at *m/z* 175, suggesting either that the chromatography of these compounds is poor or that a distinct compound at the same mass is bleeding from the column at these higher temperatures. Analysis of high resolution mass spectral data (Fig. B.2) suggests that the tailing is due to a compound with a different molecular weight, likely C₃O₃H₆, and thus the tail is neglected in the peak fits used to determine the 2,3-butanediol isomer concentrations.

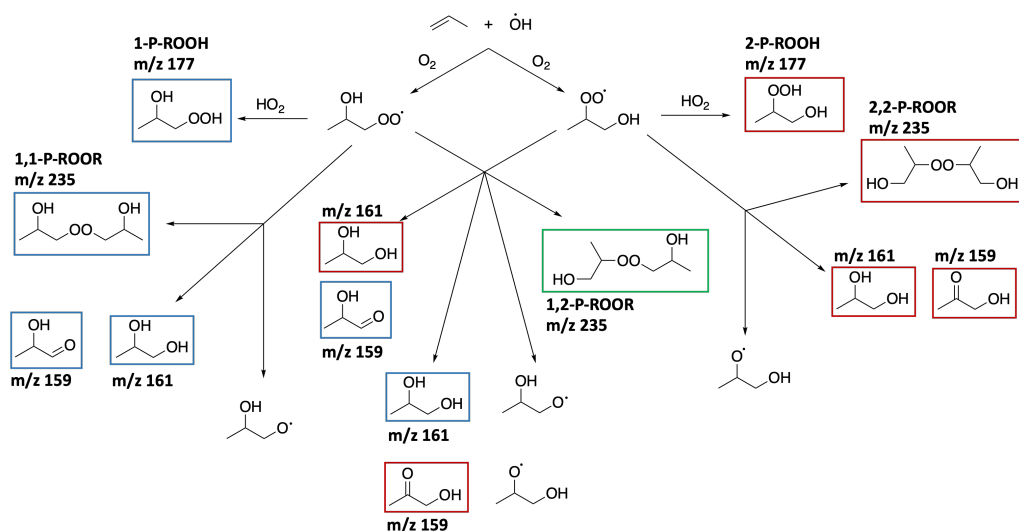
As in the analysis of the 2-methylpropene system, high HO₂ experiments ($\frac{[HO_2]}{[RO_2]} > 2$)

were performed with a mixture of ethene and cis-2-butene to directly compare the formation rates of the accretion products. The distribution of the stereoisomers of butanediol does not change (within error) under this condition, with an average distribution of 31($\pm$ 6)%/69($\pm$ 6)%. Without chromatographic separation of the stereoisomers of the ROOH products, it is difficult to draw any definitive conclusions from this observation of the butanediol isomeric distribution. In these experiments, accretion products formed in the cross reactions between the ethene- and cis-2-butene-derived peroxy radicals (m/z 235) were observed alongside accretion products resulting from the corresponding self-reactions (m/z 263), as shown in Figure 3.2d. The measured formation rates of these compounds will be discussed in the section on ROOR formation rates.

Propene

The mechanism of the OH-initiated NO_x-free propene oxidation system is given in Scheme 3.3. Two structural isomers of the propene-derived hydroxyperoxy radical are generated in the reaction of propene and OH - a primary peroxy radical (1-P) via the minor addition pathway and a secondary peroxy radical (2-P) in the major addition pathway. At sufficiently high HO₂/RO₂ concentrations, the distribution of the ROOH isomers is expected to match that of the peroxy radical isomers. However, in these experiments the HO₂/RO₂ ratio ranged from 0.2-0.4, an order of magnitude lower than that achieved in the high HO₂ oxidations of 2-methylpropene and cis-2-butene (in which the HO₂/RO₂ ratios exceeded 2). Therefore, the observed distribution is approximately 15% different than the expected distribution of the peroxy radical isomers (40($\pm$ 3)%/60($\pm$ 3)% for 1-P/2-P) (Teng, Crounse, L. Lee, et al., 2015), exhibiting an average distribution of 26($\pm$ 5)%/74($\pm$ 5)% for 1-P-ROOH/2-P-ROOH.

This distribution diverges further from the expected peroxy radical isomer distribution in experiments with high RO₂/HO₂ ratios ($\frac{[HO_2]}{[RO_2]} \ll 1$), exhibiting an average distribution of 17($\pm$ 1)%/83($\pm$ 1)%. This perturbation demonstrates, as expected, that the primary peroxy radical undergoes self- and cross-reaction more quickly than the secondary peroxy radical. However, this perturbation is less substantial than that observed for the distribution of the 1-MP-ROOH and 3-MP-ROOH, suggesting that the difference in self- and cross-reaction rates between the tertiary and primary peroxy radicals is more significant than that between the secondary and primary peroxy radical. This is consistent with previous observations that the reactivity with respect to self- and cross-reaction decreases with increasing peroxy radical substitution.



Scheme 3.3: Reaction scheme for the oxidation of propene by OH in the presence of O₂. Stable products that can be observed with the CF₃O⁻ GC-CIMS are boxed and color-coded such that products that are derived from the primary peroxy radical are in blue, those derived from the secondary peroxy radicals are in red, and products formed from the cross-reactions of the primary and secondary peroxy radicals are in green. Each products is labelled with the m/z of that product in our CIMS, which is equal to the molecular weight + 85. In the presence of O₂, the alkoxy radicals will form formaldehyde and acetaldehyde.

As in the methylpropene oxidation system, the isomer distribution of the propene-derived accretion products (1,1-P-ROOR, 1,2-P-ROOR, and 2,2-P-ROOR) is influenced by the competing effects of the peroxy radical distribution and the self- and cross-reaction rates. However the differences in these quantities across the peroxy radical isomers are less pronounced in the propene system than in the 2-methylpropene system. In experiments with high RO₂/HO₂ ratios, the accretion product formed in the cross-reaction of the primary and secondary peroxy radicals is most prominent, and is present in an average proportion of 54(±2)%. On the other hand, the 1,1-P-ROOR and 2,2-P-ROOR compounds are present in similar proportions, with an average distribution of 32(±3)%/15(±4)%.

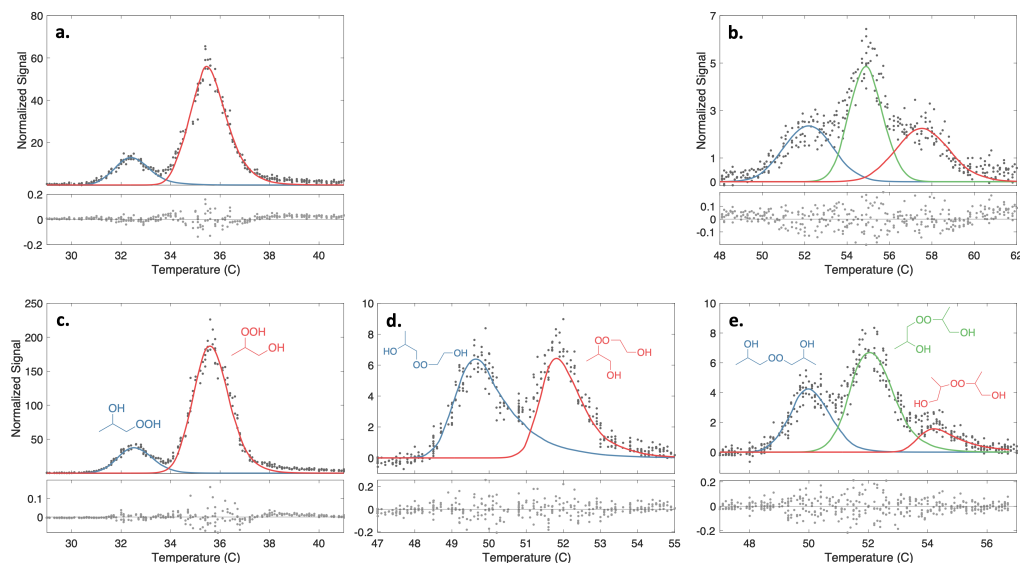


Figure 3.3: Sample gas chromatograms of several important masses produced in the oxidation of propene by OH in the presence of O₂ and ethene, including the ROOH (a and c), the ROOR formed in the self-reaction (b and e), and the ROOR formed in the cross-reaction with ethene (d). Chromatograms in the upper panel (a and b) are from experiments with high RO₂/HO₂ ratios, while those in the lower panel (c, d, and e) are from experiments with high HO₂/RO₂ ratios. The bootstrapped best-fits of the relevant peaks are plotted on top of the GC traces, and structures are given for the assignments of these peaks. Below each chromatogram the residuals of the best fits are plotted as fractions of the maximum peak signal.

In the high HO₂ system, the proportion of the total ROOR signal that is composed of 2,2-P-ROOR decreases to 10(±2)% on average. This is an effect similar to that observed in the high HO₂ regime of the 2-methylpropene system, in which the fraction of 3,3-MP-ROOR dramatically decreases due to the reaction of 3-MP with ethene-derived peroxy radicals. Therefore, 2-P also preferentially reacts with ethene-derived peroxy radicals than undergoing self-reaction, although this difference between reactivity in the cross-reaction vs. the self-reaction is less pronounced than the difference for the tertiary peroxy radical. Further, two peaks are observed at the mass of an accretion product formed in the cross-reaction of ethene-derived peroxy radicals and propene-derived peroxy radicals (*m/z* 221). These are produced with an average distribution of 65(±1)%/35(±1)%. In analogy to 1,3-MP-ROOR, due to the observed decrease in the production of 2,2-P-ROOR under these conditions, we assign the more prominent peak to 2P-E-ROOR. The production rates of these and other peroxy radicals are quantified and discussed

further in the next section.

ROOR Formation Rates

The formation rates of the various accretion products formed in these alkene oxidation systems ($k_{3,2}\alpha_{3,2d}$) were measured relative to the formation rate of the ethene-derived accretion product, as described in the Methods section. The resulting $k_{3,2}\alpha_{3,2d}$ values for the self- and cross-reactions of the various peroxy radical isomers formed in the 2-methylpropene, propene, and cis-2-butene oxidation systems (and the relevant cross-reactions with ethene) are given in Table 3.1.

In Figure 3.4, the measured $k_{3,2}\alpha_{3,2d}$ values for each of the self-reactions are plotted as a function of carbon number of the peroxy radical and color-coded by peroxy radical substitution. Despite the uncertainties in our measurements, it is clear that the formation rate of the accretion product decreases by approximately an order of magnitude as the substitution of the peroxy radical increases, with the formation of the ROOR being the fastest for primary peroxy radical self-reactions (on the order of $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and the slowest for the tertiary peroxy radical self-reactions (on the order of $10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This observation is consistent with the general observation that the overall rate of the self-reaction decreases with increasing peroxy radical substitution (Jenkin, Valorso, et al., 2019; Orlando and Tyndall, 2012) and suggests that, at least for small alkene-derived peroxy radicals, $k_{3,2}\alpha_{3,2d}$ depends strongly on peroxy radical substitution with no clear dependence on carbon number (within the error of these measurements).

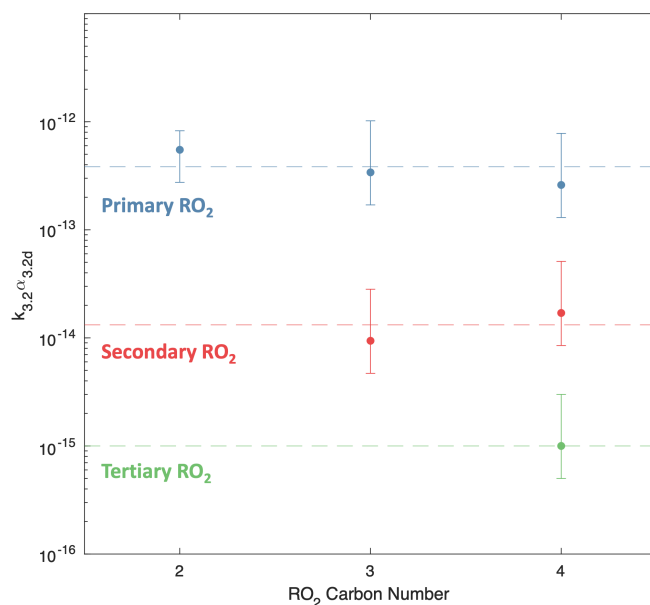


Figure 3.4: Measured values of $k_{3,2}\alpha_{3,2d}$ for the self-reactions of the ethene, methylpropene, propene, and cis-2-butene-derived peroxy radical systems, plotted as a function of carbon number of the peroxy radical and colored by substitution of the peroxy radical. Dashed lines give the average value of $k_{3,2}\alpha_{3,2d}$ for each of the primary, secondary, and tertiary peroxy radical groups.

Of the systems studied here, the self-reaction rate constants for the reactions of the 2-B (Jenkin and Hayman, 1995), 1-MP (Boyd, Lesclaux, et al., 1996; Chakir et al., 2004), and 3-MP peroxy radicals (Boyd, Villenave, and Lesclaux, 2003) have been measured in prior studies. For these systems, we use the $k_{3,2}\alpha_{3,2d}$ measured in this work and the literature value for the rate constant to estimate $\alpha_{3,2d}$, the branching fraction to the formation of the accretion product. These values are given in the third column of Table 3.1. These results suggest that for the systems discussed here, the branching fraction to the formation of the ROOR is largest in the ethene-derived primary peroxy radical self-reaction. The implied branching fraction decreases significantly for the C4 primary methylpropene-derived peroxy radical to approximately 5%, and decreases further for the self-reaction of the C4 secondary cis-2-butene-derived peroxy radical to 2%. The estimated value of $\alpha_{3,2d}$ for the C4 tertiary methylpropene-derived peroxy radical (7%) is similar to that found for the 1-MP peroxy radical.

Beyond the conclusion that $\alpha_{3,2d}$ is higher in the ethene-derived peroxy radical

Reactants	$k_{3,2}\alpha_{3,2d}$ ($\times 10^{-13}$) $\frac{\text{molec}}{\text{cm}^3\text{s}}$	$k_{3,2}$ ($\times 10^{-13}$) $\frac{\text{molec}}{\text{cm}^3\text{s}}$	Implied $\alpha_{3,2d}$
Ethene			
$\text{HOCH}_2\text{CH}_2\text{O}_2 + \text{HOCH}_2\text{CH}_2\text{O}_2$	$5.5(\pm 2.6)^{\text{a}}$	$24(\pm 10)$	$.23(\pm .05)$
Propene			
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{O}_2 + \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{O}_2$	3.4		
$\text{CH}_3\text{CH}(\text{O}_2)\text{CH}_2\text{OH} + \text{CH}_3\text{CH}(\text{O}_2)\text{CH}_2\text{OH}$	.094		
$\text{CH}_3\text{CH}(\text{O}_2)\text{CH}_2\text{OH} + \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{O}_2$	1.6		
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{O}_2 + \text{HOCH}_2\text{CH}_2\text{O}_2$	3.8		
$\text{CH}_3\text{CH}(\text{O}_2)\text{CH}_2\text{OH} + \text{HOCH}_2\text{CH}_2\text{O}_2$	2.3		
cis-2-butene			
$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3 + \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3$	.17	8.4^{b}	.02
$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}_2)\text{CH}_3 + \text{HOCH}_2\text{CH}_2\text{O}_2$	1.6		
2-methylpropene			
$(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2 + (\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2$	2.6	51^{c}	.05
$(\text{CH}_3)_2\text{C}(\text{O}_2)\text{CH}_2\text{OH} + (\text{CH}_3)_2\text{C}(\text{O}_2)\text{CH}_2\text{OH}$	.010	$.15^{\text{d}}$	.07
$(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2 + (\text{CH}_3)_2\text{C}(\text{O}_2)\text{CH}_2\text{OH}$	.80		
$(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{O}_2 + \text{HOCH}_2\text{CH}_2\text{O}_2$	3.3		
$(\text{CH}_3)_2\text{C}(\text{O}_2)\text{CH}_2\text{OH} + \text{HOCH}_2\text{CH}_2\text{O}_2$	2.1		

Table 3.1: The measured $k_{3,2}\alpha_{3,2d}$ values for each of the systems in this study. The uncertainty for all of the values measured in this work is 50%. For those systems for which the peroxy radical self-reaction rate constant has been measured, the literature value of the rate is given and the resulting implied α , calculated from the literature k value and the reported $k_{3,2}\alpha_{3,2d}$ value, is given in column 3. ^aAll values in this row are from Murphy et al. (2023). ^bJenkin and Hayman, 1995. ^cBoyd, Lesclaux, et al., 1996. ^dBoyd, Villenave, and Lesclaux, 2003.

self-reaction system than in the cis-2-butene or methylpropene-derived peroxy radical systems, within the error of these estimates no definitive conclusions can be drawn about the relationship between peroxy radical structure and $\alpha_{3,2d}$. The observed decrease in the branching fractions compared to the ethene-derived peroxy radical system may result from a variety of factors, including a decrease in the branching fraction with increasing carbon number, the branched structure of the methylpropene-derived peroxy radical as opposed to the linear structure of the ethene-derived peroxy radical, or a difference in the intersystem crossing rate of the different cis-2-butene stereoisomers (Hasan, Salo, et al., 2020). Further studies are needed to explore the relationship between structure and $\alpha_{3,2d}$.

Although $k_{3,2}$ for the propene-derived peroxy radical systems have not been measured to our knowledge, we estimate a possible range for $\alpha_{3,2d}$ and $k_{3,2}$ for the self-reactions of 1-P and 2-P using those values measured for other peroxy radical systems. First, we assign possible maximum and minimum values for the rate constant and calculate the implied $\alpha_{3,2d}$. As a maximum we assign a value of $k_{3,2}$ approximately equal to that found for the ethene-derived peroxy radical self-reaction ($k_{3,2} = 2.4 \times 10^{-12}$ molec cm⁻³ s⁻¹). This yields estimated lower limits of the branching fractions for the self-reactions of each isomer of $\alpha_{3,2d,1P} = .14$ and $\alpha_{3,2d,2P} \approx 0$. Alternatively, assigning a likely low-limit value of $k_{3,2}$ approximately equal to that found for the cis-2-butene-derived peroxy radical yields $\alpha_{3,2d,1P} = 0.40$ and $\alpha_{3,2d,2P} = 0.01$. If we instead assume, as an upper limit, that $\alpha_{3,2d} = 0.25$ (equal to that of the ethene-derived peroxy radical) for both isomers, we obtain an estimate of the rate coefficient of $k_{3,2,1P+1P} = 1.4 \times 10^{-12}$ molec cm⁻³ s⁻¹ and $k_{3,2,2P+2P} = 3.8 \times 10^{-14}$ molec cm⁻³ s⁻¹. Assuming a value closer to that of the cis-2-butene system ($\alpha_{3,2d} = 0.02$) yields a rate constant of $k_{3,2,1P+1P} = 1.7 \times 10^{-11}$ molec cm⁻³ s⁻¹ and $k_{3,2,2P+2P} = 4.7 \times 10^{-13}$ molec cm⁻³ s⁻¹. Further work is clearly required to measure either the rate constant or branching fraction for the propene-derived peroxy radical system.

In addition to the formation rates of the accretion products for the various peroxy radical isomers of each of the alkene systems, Table 3.1 also reports the measured $k_{3,2}\alpha_{3,2d}$ values for the various cross reactions of these isomers with other isomers of the same alkene-derived peroxy radicals and with the ethene-derived peroxy radicals. The relationship between the cross-reaction rates and the corresponding self-reaction rates are explored in Figure 3.5. Previously, the relationship between the self-reaction rates of two peroxy radicals and their corresponding cross-reaction rate has been suggested to be two times the geometric mean of the self-reaction rates (Equation 3.11) (Jenkin, Valorso, et al., 2019; Orlando and Tyndall, 2012; Madronich and Calvert, 1990):

$$k_{3,2,R+R',geo} = 2\sqrt{k_{3,2,R}k_{3,2,R'}} \quad (3.11)$$

The relationship between the geometric mean of $k_{3,2,R}\alpha_{3,2d,R}$ and $k_{3,2,R'}\alpha_{3,2d,R'}$ and the measured $k_{3,2,R+R'}\alpha_{3,2d,R+R'}$ for a variety of peroxy radical cross-reactions is given in the left panel of Figure 3.5.

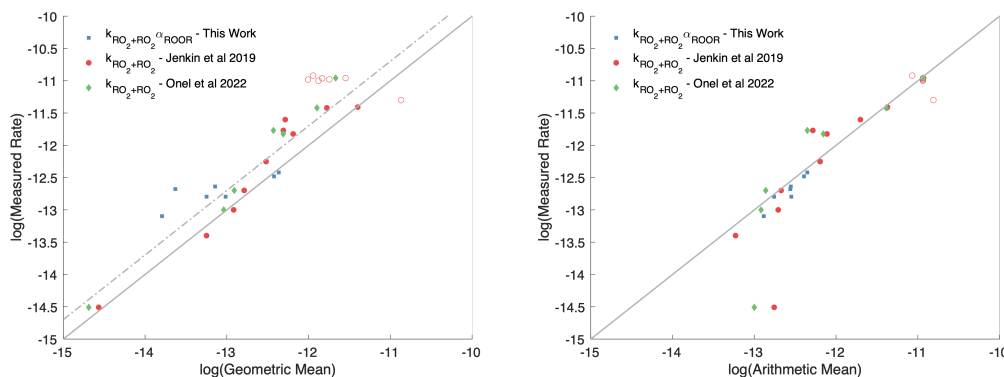


Figure 3.5: The relationship between the self-reaction and cross-reaction rate constants for the peroxy radical systems given in Jenkin et al. 2019 (red circles), and the relationship between $k_{3,2}\alpha_{3,2d}$ values for the self- and cross-reactions examined in this study (blue squares). Open red circles denote data from Jenkin et al. that correspond to a cross-reaction that involves at least one acyl peroxy radical. The left panel shows the relationship between the measured cross reaction rates and the geometric mean of the measured self-reaction rates, while the right panel shows the relationship between the measured cross reaction rates and the arithmetic mean of the measured self-reaction rates. Green diamonds use the self-reaction rate for CH_3O_2 given in Onel et al. instead of that given in Jenkin et al. Solid gray lines give the 1:1 line, while the dashed gray line is the 2:1 line.

These data are compared to the relationship between the geometric means of the measured self-reaction rate constants and the measured cross-reaction rate constants given in Jenkin et al. 2019 in the left panel of Figure 3.5. In green diamonds, the geometric means of the cross-reactions that include CH_3O_2 as a reaction partner are calculated using the most recently measured value of the self-reaction rate constant for CH_3O_2 given in Onel et al. ($2.0(\pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), which is approximately 40% slower than the previously recommended value as given in Jenkin et al. (Onel et al., 2022). In the right panel of Figure 3.5, the relationship between the measured cross-reaction rates and the arithmetic mean of the self-reaction rates (Equation 3.12) is also plotted with the 1:1 line:

$$k_{3,2,R+R',ar} = \frac{k_{3,2,R} + k_{3,2,R'}}{2} \quad (3.12)$$

These plots suggest that, while twice the geometric mean has been suggested previously as a method for estimating the cross-reaction rates of peroxy radical systems, the arithmetic mean equally captures this relationship. There is a clear outlier in

this trend, the cross-reaction of the tert-butylperoxy radical ($\text{t-C}_4\text{H}_9\text{O}_2$) with the methyl peroxy radical (CH_3O_2). However, the recommended rate coefficient for this reaction is fairly uncertain, and therefore this outlier should not rule out the arithmetic mean as a possible method for estimating the cross reaction (Parkes, 1975; Osborne and Waddington, 1984; Atkinson et al., 2006). Indeed, in this study, a simple photochemical box model run of these systems with the cross-reactions given by the arithmetic mean matches the data more closely than a similar run using the geometric mean or twice the geometric mean as the cross-reaction rate. The addition of the factor of two in 3.11 adds the additional curiosity that in the limiting case where $\text{R}'=\text{R}$, $k_{3,2,\text{R}}=2k_{3,2,\text{R}}$. Clearly, further work is needed to develop a robust relationship between the self- and cross-reactions of a variety of peroxy radicals for use in models.

3.4 Conclusion

The kinetics and products of the bimolecular reactions of peroxy radicals in low NO_x environments, including peroxy radical self- and cross-reactions, are crucial to quantify if the ultimate fate and influence of peroxy radical chemistry is to be fully understood. Despite recent increased study of the peroxy radical self-reaction and the formation of the accretion product via this self-reaction, there is still little information about the formation of this accretion product as a function of structure. In this study, we have added to the current knowledge of these reactions by examining the formation of accretion products in the self- and cross-reaction in primary, secondary, and tertiary peroxy radicals derived from the oxidation of small alkenes by OH. We find that the formation rate of the accretion product depends largely on the substitution of the peroxy radical and decreases with increasing substitution, with no clear dependence on carbon chain length. Further, the formation of the accretion product in the cross-reaction systems yielded formation rates that are well-described by the arithmetic mean of the corresponding self-reactions.

Chapter 4

A CENSUS OF ORGANIC NITROGEN IN THE LOS ANGELES ATMOSPHERE

4.1 Introduction

Nitrogen oxides ($\text{NO}_x = \text{NO}_2 + \text{NO}$), emitted primarily via lightning or anthropogenic and biogenic combustion processes, play a significant role in the chemistry of the troposphere. In the major daytime radical cycling pathway of NO_x , NO_2 is photolyzed to NO and oxygen atoms, which then react with O_2 to form ozone (O_3). Reaction of NO with O_3 then reforms NO_2 . This sets up, during the daytime, a steady-state ratio $[\text{NO}_2]/[\text{NO}]$ of between 1 and 10 in the boundary layer. Occasionally, NO reacts with organic peroxy radicals (RO_2) or hydroperoxy radicals (HO_2) to regenerate NO_2 . By breaking the O_2 bond in the RO_2 , this process results in the net formation of O_3 , an oxidant and greenhouse gas that is harmful to human health (Beaver et al., 2012; J. Zhang, Wei, and Fang, 2019) (Reactions 4.1-4.3).



In addition to these radical propagation cycles, NO_x will undergo a series of radical termination reactions, leading to the formation of mono- and multi-functional organic nitrates (RONO_2) or nitroaromatic compounds. While these nitrogen containing organic compounds can act as sinks of NO_x , either by deposition or gas-particle partitioning, they can also undergo transport to locations removed from the original source and re-release NO_x via photolysis or further reaction (Beaver et al., 2012; Teng, Crounse, L. Lee, et al., 2015). Therefore, quantification of the formation and fate of organic nitrogen chemistry is important for properly modelling NO_x chemistry locally, regionally, and globally.

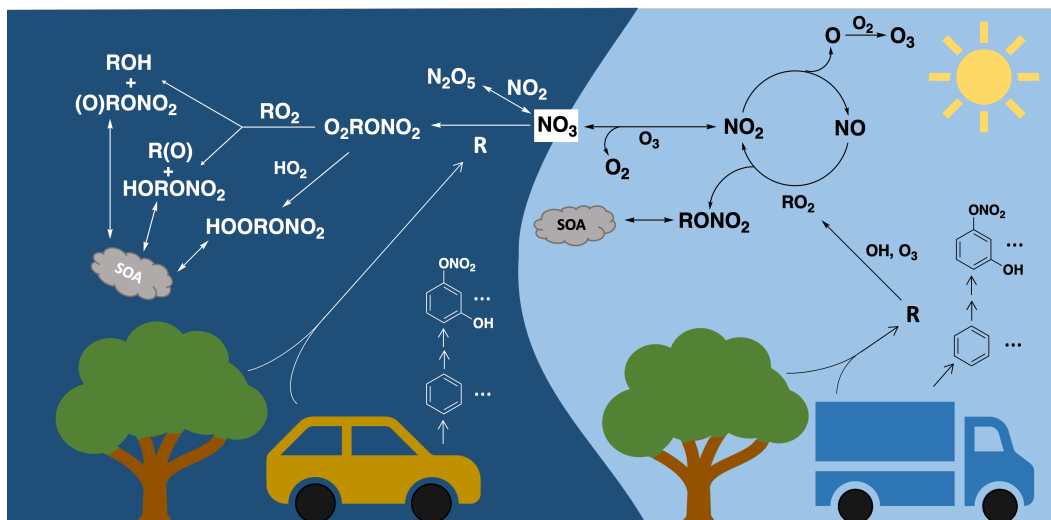


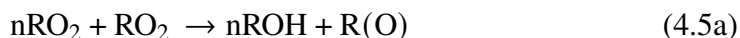
Figure 4.1: Simplified scheme showing the NO_x radical cycle and reactions leading to the formation of organic nitrogen during the daytime (right panel) and the nighttime (left panel).

During the daytime, the formation of RONO₂ primarily proceeds by reaction of NO with RO₂ (Figure 4.1). These RO₂ are typically produced in the OH-initiated oxidation of hydrocarbons, either via OH and subsequent O₂ addition to a double bond (in which case reaction with NO forms β -hydroxy nitrates) or, following hydrogen abstraction and subsequent O₂ addition (in which case reaction with NO forms an alkyl nitrate). The reaction of RO₂ with NO, in addition to forming RONO₂ in minor yield, can also lead to the formation of an alkoxy radical (RO) and NO₂:



For sufficiently large RO, hydrogen-shift chemistry followed by O₂ addition and subsequent reaction with NO can also yield hydroxy nitrates where the substitutions are four or more carbon atoms apart. The measured yields of RONO₂ from the reaction of RO₂ with NO range between 0.1-35% and depend largely on the stability of the ROONO* intermediate (Perring, Pusede, and Cohen, 2013). In general, RONO₂ yields increase with carbon number and pressure, and decrease with temperature. Aromatics and highly oxygenated compounds tend to have much lower nitrate yields (Praske et al., 2015; Xu, Møller, Crounse, Kjaergaard, et al., 2020).

In addition to the daytime formation pathway, organic nitrates are formed at night via addition of NO_3 and, subsequently O_2 , to a double bond to form a nitrooxy peroxy radical (nRO_2). These nRO_2 subsequently react with HO_2 yielding hydroperoxides or with other RO_2 to produce both carbonyl and hydroxy nitrates:



where nROH is a hydroxy nitrate and $\text{nR}(\text{O})$ is a nitrooxy carbonyl. In many laboratory experiments, including some described here, the nRO_2 react with NO_3 yielding, typically, alkoxy radicals which can undergo scission reactions. Although reaction with NO_3 generally accounts for a smaller fraction of the total atmospheric oxidation of hydrocarbons than reaction with OH , the yield of the hydroxy nitrate is much higher for these reactions (with yields of up to 80%) (Hallquist et al., 1999; Fry, Kiendler-Scharr, et al., 2009). Therefore, under some conditions, these reactions account for up to 50% or more of the total RONO_2 formed (Perring, Pusede, and Cohen, 2013).

The measurement of RONO_2 has historically been quite difficult, due to the high degree of functionalization and the wide variety of RONO_2 present in the atmosphere. The development of thermal dissociation laser-induced-fluorescence methods (TD-LIF) to measure total alkyl nitrate concentrations greatly improved the study of ambient nitrate chemistry and the technique has been utilized to measure the (previously underestimated) role of RONO_2 chemistry in several regions (Perring, Pusede, and Cohen, 2013). However, the importance of measuring individual RONO_2 cannot be discounted, as RONO_2 of varying sizes and with varying functional groups will have different atmospheric fates. For example, nitrates that are highly functionalized are more likely to partition to aerosol due to their decreased volatility, while nitrates that retain a double bond are more likely to undergo further oxidation (Perring, Pusede, and Cohen, 2013). Additionally, measurements of the relative concentrations of various RONO_2 can provide significant insight into the local chemistry of a region. For example, while Beaver et al. found that biogenically-derived nitrates accounted for approximately two-thirds of the total alkyl nitrates in a forested region near Sacramento during the 2009 BEARPEX campaign, Teng et al. found that the nitrate chemistry of small alkenes plays a significant role in oxidant formation in Houston (Beaver et al., 2012; Teng, Crounse, L. Lee, et al., 2015). On the other hand, at the Bakersfield supersite during the CalNex campaign in 2010, VOC measurements were used to estimate that long-chain alkanes from anthropogenic sources were the

largest source of alkyl nitrates during the day, followed by isoprene, aromatics, and alkenes, while monoterpenes dominated nighttime formation of alkyl nitrates with small contributions from isoprene and alkenes (Rollins, Pusede, et al., 2013). Thus, the prominence of various precursors in nitrate chemistry varies drastically by location and time of day. Speciation of ambient alkyl nitrates can further elucidate the importance of competing formation pathways of nitrate products, such as the formation of nitrooxy-hydroperoxide compounds from $\text{RO}_2 + \text{HO}_2$ chemistry at night (Schwantes et al., 2015). Therefore, measurements of individual alkyl nitrates and their relative importance in various regions are necessary to better constrain nitrate chemistry and how it differs across various environments.

In addition to the effects of nitrate chemistry on oxidant formation, the formation of low-volatility organic nitrates can lead to the growth of secondary organic aerosol (SOA). Previous ambient measurements have demonstrated that the organic nitrates formed in the gas-phase are significant components of organic aerosol mass, with organonitrate groups estimated to contribute up to 10% of total organic mass in submicron particles in some regions (Day et al., 2010; Fry, Draper, et al., 2013). The contribution of nitrates to aerosol loading appears to be especially important during the night, where NO_3 -derived organic nitrates have been measured to constitute as much as one-third of nighttime increases in organic aerosol (Fry, Draper, et al., 2013; B. H. Lee, Mohr, et al., 2016; Rollins, Browne, et al., 2012). A strong connection between the concentrations of VOC precursors and corresponding particulate organic nitrate has been observed, further demonstrating that the organic nitrates formed in the gas-phase processes discussed above are likely to partition into the particle phase (B. H. Lee, Mohr, et al., 2016). However, the contribution of organic nitrates throughout the diurnal period has not been measured in a variety of regions, and the effect of NO_x reductions in major cities due to emissions regulations is not well understood.

In this work, we aim to create a census of the important functionalized organic nitrogen-containing compounds present in the Los Angeles urban atmosphere during the 2021 RECAP-CA campaign. We examine the composition of these compounds and, by comparison to laboratory data, identify several of the compounds observed in the ambient gas-phase atmosphere. We then examine the roles played by biogenic hydrocarbons, alkenes, and aromatic compounds in the nitrogen budget of the urban atmosphere in this region.

4.2 Methods

Sampling Period and Location

The Re-Evaluating the Chemistry of Air Pollutants in California (RECAP-CA) campaign took place between June and August during the summer of 2021 on the Caltech campus in Pasadena, California (34.14°N, -118.13°W). The suburban location is approximately 18 km northeast of downtown Los Angeles and 7 km south of the San Gabriel mountain range, with prevailing winds during the day coming from the south. Anthropogenic NO_x emissions from downtown Los Angeles heavily influence the chemistry at this site, with an average daytime NO value of 1.7 ppb and an average NO₂ to NO ratio of 7.7 measured during the time period examined here (Figure 4.2). Additionally, biogenic VOC emissions play a significant role in the chemistry, with local vegetation emitting copious amounts isoprene and monoterpenes, especially at high ambient temperatures. We therefore expect both NO_x chemistry and isoprene chemistry to be prominent at the site.

The Caltech gas chromatograph chemical ionization high resolution time-of-flight mass spectrometer (GC-HRToF-CIMS) and compact time-of-flight mass spectrometer (CToF-MS), which are described below, were both deployed on the second floor of the Linde Laboratory on the southwest corner of the campus. Both instruments were housed inside an unused office space with a joint Teflon inlet, approximately 2m long, sampling outside of the window, at a height of approximately 7 m from the ground. Very high flows were maintained through this inlet such that the residence time was approximately 0.1s. The CToF sampled from the inlet between August 4th, 2021 and September 5th, 2021, while the GC-CIMS sampled between August 9th, 2021 and September 7th, 2021. In this study, we focus on the time period between August 28th, 2021 and September 5th, 2021, as this period encompassed the overlap of both high quality GC-CIMS data and high quality CToF data. The average daily maximum temperature during this time period was 33.2°C, with an average daily minimum temperature of 18.6°C. The relative humidity (RH) was 57% on average, with an average daily maximum RH of 76% at night and a minimum daily average RH of 30% typically reached in the mid afternoon (Figure 4.2).

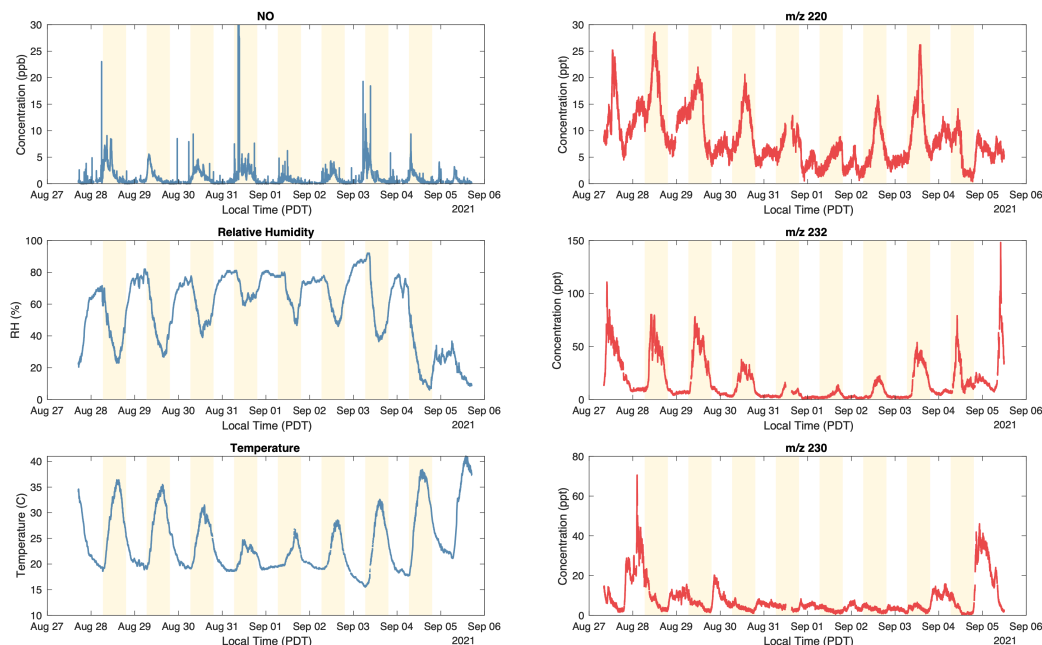


Figure 4.2: Daily conditions at the sampling site between August 28th, 2021 and September 5th, 2021 compared to concentrations of representative compounds measured with the Caltech CToF-CIMS. NO concentration (ppb, upper left panel) and temperature ($^{\circ}\text{C}$, lower left panel) measurements were conducted at the California Institute of Technology Air Quality Station (CITAQS). NO concentrations were measured in the CITAQS with a Teledyne T200U. Note that, on August 31st at approximately 8:45 AM PDT, there NO concentration spiked to a value of approximately 220 ppb. This spike was due to a truck idling beside the sampling area. Relative humidity (RH, %, middle left panel) was measured by the TCCON weather station on top of the Linde Laboratory using a Vaisala HMP60 temperature and humidity probe. Concentrations, in ppt, of compounds present at m/z 220 (e.g. C4 hydroxy nitrates, upper right panel), m/z 232 (e.g. isoprene-derived hydroxy nitrates, middle right panel), and m/z 230 (e.g. isoprene-derived nitrooxy carbonyls, lower right panel) as measured by the CToF-CIMS are shown for comparison. Structures corresponding to compounds observed at m/z 220 are given in Table 4.3, structures corresponding to compounds observed at m/z 232 are given in Table 4.1, and structures corresponding to compounds observed at m/z 230 are shown in Table 4.2. Yellow shaded rectangles show the periods between sunrise and sunset on each day.

Instrumentation

GC-HRToF-CIMS

The Caltech GC-HRToF-CIMS has been described in detail elsewhere (Vasquez, Allen, et al., 2018), but a brief description and the details of operation during the campaign are given here.

The HRToF-CIMS uses CF_3O^- as a reagent ion, a soft ionization method that is particularly sensitive to multifunctional organic compounds (Hytinen et al., 2018). The reagent ion is produced by passing CF_3OOCF_3 gas, diluted with N_2 , through a tube coated with polonium-210. Although the GC-CIMS can be operated in direct sampling mode such that gas is sampled directly into the HRToF, during the time period discussed here the HRToF-CIMS exclusively sampled the effluent of the GC. The metal-free GC consists of a 2m fused silica column (Restek RTX-1701) that is cooled with the expansion of liquid CO_2 and heated with resistance heaters controlled with a Watlow temperature controller. Approximately 4000 sccm of ambient air was sampled from the main inlet via a 1 inch O.D. Teflon tube and directed towards the GC. The GC sub-sampled approximately 1200 sccm from this flow every hour for either 2 or 15 minutes. The flow was then diluted with 1440 sccm of N_2 , diluting the sample by a factor of 10. Analytes were trapped on a small length of column at -10°C prior to the 2m GC column. When trapping was complete, the temperature of the GC and the trap was increased from -10°C to 20°C at $13^\circ\text{C}/\text{min}$, from 20°C to 50°C at $3^\circ\text{C}/\text{min}$, and from 50°C to 130°C at $10^\circ\text{C}/\text{min}$. A flow of 5 sccm of N_2 flowed through the column during this elution period, and another 200 sccm of flow directed the column output to the ion source. To maximize the signal-to-noise ratio, the column output was flowed directly through the ion source, intersecting with 180 sccm of N_2 flowing through the ion source and 1500 sccm of N_2 from the Teflon-coated quartz flow tube. Here, the analytes react with the reagent ion, with most of the analytes forming ionized clusters with CF_3O^- (for more acidic analytes, fluorine transfer reactions may also occur). The ionized analytes are then directed into the mass spectrometer by a conical hexapole ion guide, where they are subsequently detected at a mass-to-charge ratio of their molecular weight plus the mass of CF_3O^- ($m/z = \text{mw} + 85$) or their molecular weight plus the mass of fluorine ($m/z = \text{mw} + 19$). After reaching 130°C , the column temperature was held constant for two minutes before cooling back to -10°C to repeat the sampling. This procedure was fully automated and for the time period analyzed here samples were taken throughout the day and night, with occasional short pauses for maintenance

procedures or data reduction.

In some cases, individual peaks in the ambient chromatograms were integrated to determine the contributions of individual compounds to the overall sum of the signal at a given mass. Each peak was fit to an exponentially-decaying gaussian peak shape using a modified Matlab peak fitting function (O'Haver, 2017). For each peak, the elution time was fixed (to within ± 2 seconds), and the peak widths and exponential decay constants were varied randomly to within 30-50% of the initial guess over 50-1,000 trials to determine the parameters that minimized the total error of the fit. The area under the fitted peak was then compared to the overall signal at a given mass to determine the percent contribution of the peak to the overall signal. Further discussion of the fitting procedures and the results of the bootstrap best fits that were used in the following analysis are given in Appendix C.6.

CToF-CIMS

The CToF-CIMS uses an ionization scheme identical to that described above. The instrument was essentially unchanged from the configuration described by Allen et al. (Allen, Bates, et al., 2022; Allen, Crounse, et al., 2022) and Xu et al. (Xu, Crounse, et al., 2021) except that the external aircraft inlet was replaced by the 2m Teflon tube discussed above. A large exhaust fan was utilized following the variable aperture leading to the vacuum system to keep the residence time in the external ambient inlet very short (0.1 s). The CToF does not have chromatography and the mass resolution of the mass filter is approximately four times lower than the GC-HRToF.

Instrument Calibration

The sensitivity of the CToF-CIMS to several compounds discussed here, including isoprene hydroxy nitrate, has been measured previously in our laboratory by comparison to synthetic standards (Nguyen et al., 2014; L. Lee et al., 2014). The relative sensitivity of the CToF-CIMS to other compounds, including isoprene nitrooxy-carbonyl and isoprene nitrooxy hydroperoxide, have been estimated using theoretical calculations of the relative rates of ion-molecule reactivity (Kwan et al., 2012; Paulot, Crounse, et al., 2009). Due to the wide range of compounds studied here, the lack of authentic standards for most of these compounds, and the difficulty of synthesizing authentic standards, the sensitivity of the GC-HRToF-CIMS to the compounds analyzed in this work were scaled from the observations made using the

CToF-CIMS. To determine a multiplicative factor for the relationship between the sensitivities of the two instruments, we compared the average diurnal signal of m/z 232 (the signal dominated by isoprene hydroxy nitrates) in the CToF-CIMS and the GC-HRToF, and found that the CToF-CIMS was approximately 1.4 times more sensitive to these compounds than the GC-HRToF-CIMS. This ratio was then used to estimate the sensitivity of the GC-HRToF-CIMS by comparison to the CToF-CIMS sensitivity (either calculated or measured, where available) for all of the compounds discussed in this work. A table of these sensitivities is included in Appendix C.5.

Using CF_3O^- as a reagent ion, organic compounds containing a single nitrogen atom are observed at even m/z . Some signal from the ^{13}C and ^{17}O isotopologues of non-nitrogen containing compounds also contribute to this signal. In the following analysis, these contributions are estimated using the signal at $m/z-1$ and an estimate of the isotope ratio based on the mass, and subsequently subtracted from the signal at the even m/z .

Laboratory Experiments

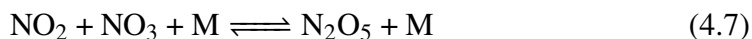
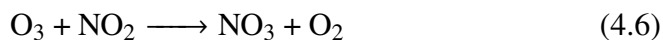
Laboratory oxidation experiments were performed to assign the elution temperatures for several organic nitrates expected to be observed in the ambient data. Two experiment types, ‘light’ and ‘dark’ oxidation experiments, were performed for several precursor alkenes. The general procedures for both of these experiments are described below.

In the ‘light’ oxidation experiments, oxidation of precursor alkenes by OH was initiated via the photolysis of H_2O_2 at 254 nm. In a typical experiment, 1000 ppb of H_2O_2 , between 50 and 500 ppb of the precursor alkene, and 1000 ppb of NO were injected into the 800-liter FEP Teflon environmental chamber. Under these conditions, OH addition followed by O_2 addition to the precursor alkenes leads to formation of a suite of peroxy radicals, which react with NO to form hydroxy nitrates (Reaction 4.4a). To create these conditions, H_2O_2 (30% by weight, Macron Fine Chemicals) was injected into the chamber by weighing the desired amount into a pre-weighed three-way glass vial and flowing air through the vial and into the chamber at a rate of 20 SLM. To ensure that the evaporation of the sample was complete, the vial was reweighed after the injection. NO was measured into a 500 mL glass bulb using manometry, with the bulb attached in series with a vacuum/ N_2 dilution system and a tank of 1993 ppm NO (Matheson). The desired concentration, typically 1000 ppb, was then reached by serial dilution, with pressure measurements

conducted by MKS 1000 and 10 Torr baratron pressure transducers. The purity of the NO sample was confirmed by obtaining an IR spectrum of the resulting bulb contents in a 19 cm pyrex FTIR cell with CaF₂ windows. The NO was then injected (prior to initiation of photolysis) by flowing dry air at 20 SLM through the bulb until the contents of bulb were flushed into the environmental chamber.

Eight Sankyo Denki 254 nm lamps were energized for 1-5 minutes to photolyze the H₂O₂ and initiate the alkene oxidation. In many of the experiments, multiple precursor alkenes were oxidized simultaneously for efficiency. The details of individual experiments are given in Appendix C.4 - these 'light' oxidation experiments were performed with propene ($\geq 99\%$, Sigma Aldrich), ethene ($\geq 99.5\%$, Sigma-Aldrich), isoprene (99%, Sigma Aldrich), 1-butene ($\geq 99\%$, Sigma Aldrich), 2-methylpropene (99%, Sigma Aldrich), 1-pentene ($\geq 98.5\%$, Sigma-Aldrich), pentane (98%, Sigma-Aldrich), and hexane ($\geq 99\%$, Sigma-Aldrich). With the exception of trapping time and sample dilution, which were altered due to the significantly higher abundance of nitrates and lower water concentrations under the laboratory conditions, all gas chromatograms in these experiments were performed under the same conditions as those performed in the field. All GC conditions used in these experiments are given in Appendix C.4.

In the 'dark' oxidation experiments, NO₃ was formed via the reaction of NO₂ and O₃ (Reactions 4.6-4.7).



In a typical experiment, the chamber was first filled with 40 liters of dry air. Following this, between 50-100 ppb of O₃ was injected using an O₃ generator (Enmet, Model 04051-011) flowing at 1.5 SLM. Simultaneously, the O₃ concentration was monitored using a Teledyne 400E Photometric O₃ Analyzer sampling at 1.5 SLM, thus ensuring that the total volume of air in the chamber did not change during this injection step. The ozone generator was turned off when the desired concentration was reached. With the O₃ instrument still sampling, a further 160 liters of dry air was injected into the chamber at 20 SLM. Once the ozone concentration in the chamber was stabilized following this dilution step, direct sampling from the CIMS instrument was initiated and NO₂ was injected into the chamber, leading to the immediate formation of N₂O₅ and NO₃. NO₂ was measured into a 500 mL glass bulb in the same manner described above for NO, and injected by flushing the bulb

with dry air at 20 SLM into the environmental chamber. Following the injection of NO_2 , a background GC was taken of the chamber contents, using the same GC conditions as described for the ‘light’ oxidation experiments (Appendix C.4). Upon completion of this GC, direct sampling was once again initiated and approximately 50-500 ppb of the precursor alkenes were injected. The alkenes were measured into a 500 mL glass bulb in the same manner described for NO and NO_2 , and injected by flushing the bulb with dry air into the environmental chamber at 20 SLM. Oxidation began immediately upon injection of the precursor alkenes - ‘dark’ oxidation studies were performed with 2-methylpropene (99%, Sigma Aldrich), cis-2-butene ($\geq 99\%$, Sigma Aldrich), propene ($\geq 99\%$, Sigma Aldrich), 2-methyl-2-butene ($\geq 99\%$, Sigma Aldrich), isoprene (99%, Sigma Aldrich), 2-methyl-1-butene (analytical standard, Fluka), 1,3-butadiene ($\geq 99\%$, Sigma Aldrich), α -pinene ($\geq 99\%$, Sigma Aldrich), 2-methyl-2-pentene ($> 98\%$, Fluka), cis-2-pentene (98%, Sigma Aldrich), 1-butene ($\geq 99\%$, Sigma Aldrich), and furan ($\geq 99\%$, Sigma Aldrich). Two minutes after the alkene injection, a GC of the system was taken. A second GC was taken approximately 50 min after the first, once the reaction had progressed further. Due to the complexity of the products in these experiments, hydrocarbons were generally injected individually rather than in groups, as was sometimes done in the case of the ‘light’ oxidation experiments. In these experiments, the nitrooxyperoxy radicals react with both NO_3 and HO_2 , with the latter formed via the decomposition of the organic alkoxy radicals. Consistent with formation of significant amounts of HO_2 , formation of hydroperoxynitrate, HO_2NO_2 , is observed in these experiments.

4.3 Results and Discussion

Diurnal Profiles

The average diurnal profiles of the concentrations of organic nitrates at several representative even m/z , measured with both the GC-CIMS and the CToF, are shown in Figure 4.3. These diurnal profiles match quite closely across both instruments throughout the observation period. For compounds at lower mass-to-charge ratios, such as m/z 206 (hydroxynitrates from the oxidation of propene), the measured GC concentrations tend to be lower than those measured by the CToF. This observation is consistent with inefficient trapping of the more volatile nitrates at the relatively high trapping temperatures used during the campaign. For example, in the laboratory, we find that the trapping efficiency of propene-derived hydroxy nitrates (m/z 206) is approximately 45% under the conditions used during the campaign, consistent with the difference in the average measured GC and CToF concentrations at m/z 206 in

the ambient data (Figure 4.3a).

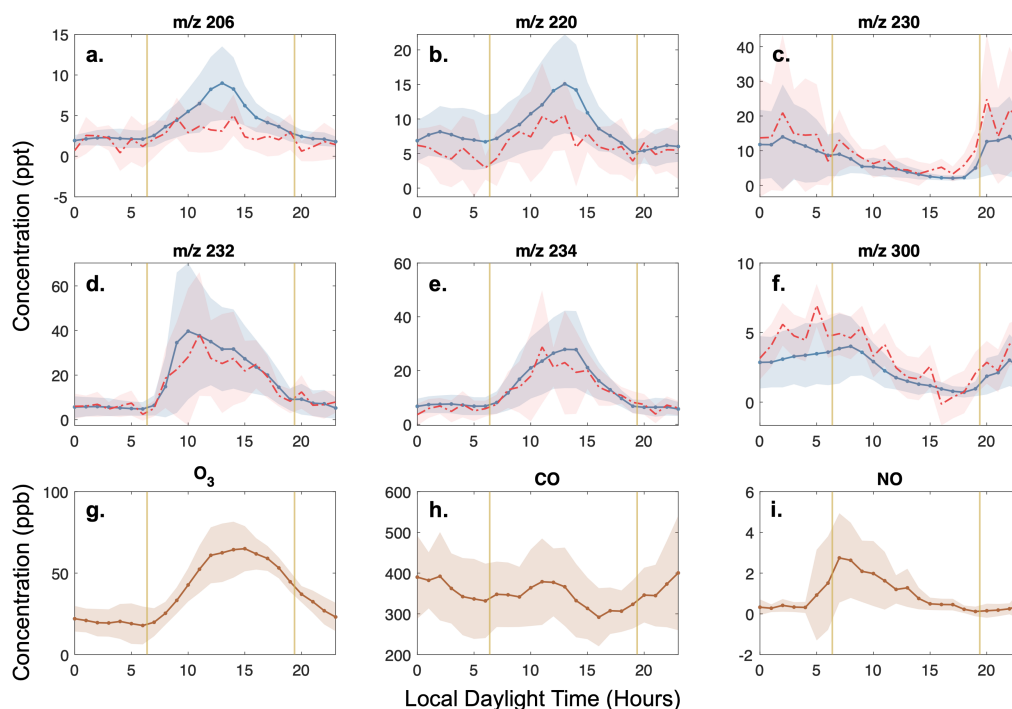


Figure 4.3: Average diurnal profiles of representative masses from August 28th - September 5th. Top two panels (a-f) show the average diurnal profiles (in pptv) of representative masses from August 28th - September 5th, measured with both the GC-CIMS (in red) and the CToF (in blue). m/z 206 (a) corresponds to the mass of propene-derived hydroxy nitrates, m/z 220 (b) are C4-derived hydroxy nitrates, m/z 230 (c) is the mass of isoprene-derived nitrooxy carbonyls, m/z 232 (d) are the isoprene-derived hydroxy nitrates, m/z 234 (e) includes C5 hydroxy nitrates and MVK/MACR-derived nitrates, and m/z 300 (f) includes monoterpene-derived hydroxy nitrates. The shaded area encompasses 1σ over the time period. Yellow vertical lines denote the local sunset and sunrise times. The lower panel (g-i) gives the average diurnal profiles (in ppbv) of O_3 , CO, and NO as measured by the CIT-AQS during the same time period, with the shaded area showing 1σ .

The diurnal profiles seen in Figure 4.3 generally fall into two categories: signals composed primarily of nitrogen containing organic compounds formed during the daytime (NCOC-day) and nitrogen containing organic compounds formed during the nighttime (NCOC-night). In general, NCOC-day increase at sunrise (between 5 and 8 AM local time), with a peak in the afternoon, followed by a steady decrease throughout the late afternoon and evening until reaching nighttime concentrations that are typically less than 1/3 those observed during the daytime. As the sun sets at

approximately 6 PM, there is a sudden increase in NCOC-night followed by a steady increase throughout the evening and a steady decrease during the daytime. At some m/z (such as m/z 248), both NCOC-day and NCOC-night contribute significantly to the overall signal, leading to more complicated diurnal profiles. The approximate times of sunset and sunrise during the time of the campaign are shown as vertical lines on the figures. For the majority of this analysis, ‘daytime’ refers to the time period between 8:00 AM and 8:00 PM, whereas ‘nighttime’ refers to the time period between 8:00 PM and 8:00 AM – where different definitions are used, the difference is noted.

The chromatographic data show that the NCOC-day and NCOC-night shown in Figure 4.3 are composed of a large number of compounds that contribute to the signal at a given mass-to-charge ratio. In the next sections, we identify some of the individual compounds that contribute to NCOC-day and NCOC-night and touch upon the implications for urban organic nitrate chemistry.

Biogenic Nitrates

As is evident in Figure 4.4, organic nitrogen compounds derived from the oxidation of biogenic hydrocarbons (including isoprene-derived and monoterpene-derived NCOC) contribute a significant fraction of the total concentration of gas-phase organic nitrates observed during the time period discussed here. The total contribution of the sum of isoprene- and terpene-derived organic nitrates peaked during the morning at an average of 35% of the total signal observed at even m/z . This contribution increased to approximately 37% of the total signal at even m/z on days with maximum temperatures greater than 30°C. Of the gas-phase biogenic nitrates identified here, the nitrates of isoprene contributed most significantly to the total organic nitrate concentration, carrying 33% of the total signal observed at even m/z during this time period. The prominence of biogenic emissions in observed gas-phase organic nitrogen formation is generally consistent with analyses of emissions in June of 2021, which found that up to 60% of total VOC OH reactivity, ozone formation potential, and SOA formation potential could be attributed to emissions of biogenic terpenoid compounds and that this contribution is most significant at high temperatures (Pfannerstill et al., 2024). However, although in both studies biogenic compounds are observed to be prominent, the estimated contribution of these biogenic compounds appears to be higher in the analysis of Pfannerstill et al. than the contribution to the overall organic nitrogen budget observed in this study. This is likely due in part to the rapid hydrolysis of isoprene-derived hydroxy

nitrates (Vasquez, Crounse, et al., 2020), which leads to an underestimate of the total isoprene hydroxy nitrates formed in the gas-phase.

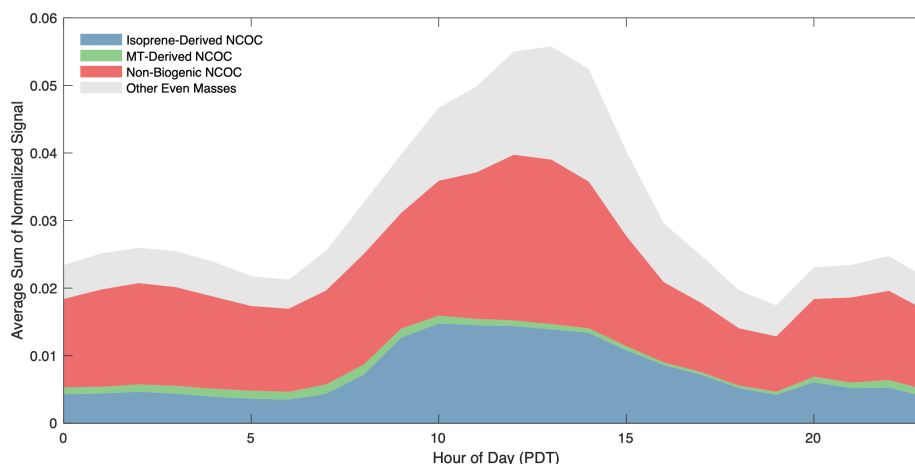


Figure 4.4: The average total signal observed in the CToF-CIMS at isoprene-derived nitrate masses (m/z 232, 40% of m/z 230, m/z 248, and 49% of m/z 234) in blue, monoterpene(MT)-derived nitrate masses (m/z = 298, 300, and 316) in green, and other non-biogenic nitrates (m/z = 158, 172, 190, 192, 204, 206, 218, 220, 60% of 230, 51% of 234, 236, 246, 250, and 264) in red, as a function of hour of day over the time period examined here. The average sum of the signal at other even masses is given in grey. The signals at m/z 230 and m/z 234 are split across categories as they contain multiple organic nitrate products with different sources. These breakdowns are discussed further in the main text.

Hydroxy Nitrates of Isoprene (IHN)

Isoprene-derived hydroxy nitrates (mw 147) are observed at m/z 232 in our CF_3O^- CIMS. The diurnal profile of the signal at m/z 232 (Figure 4.3d) is consistent with products primarily formed during the daytime, with the average concentration reaching a peak of approximately 40 ppt at 10 AM. The lower panel of Figure 4.5 shows a sum of the ambient chromatograms taken on 08/28/2021 during both the daytime and the nighttime, with the nighttime ambient data multiplied by a factor of four for clarity. These traces are largely representative of the ambient chromatographic data at m/z 232 observed throughout RECAP. The daytime signal is dominated by two compounds, eluting at 73.1°C and 77.8°C, while at night the signal is carried by a variety of other compounds.

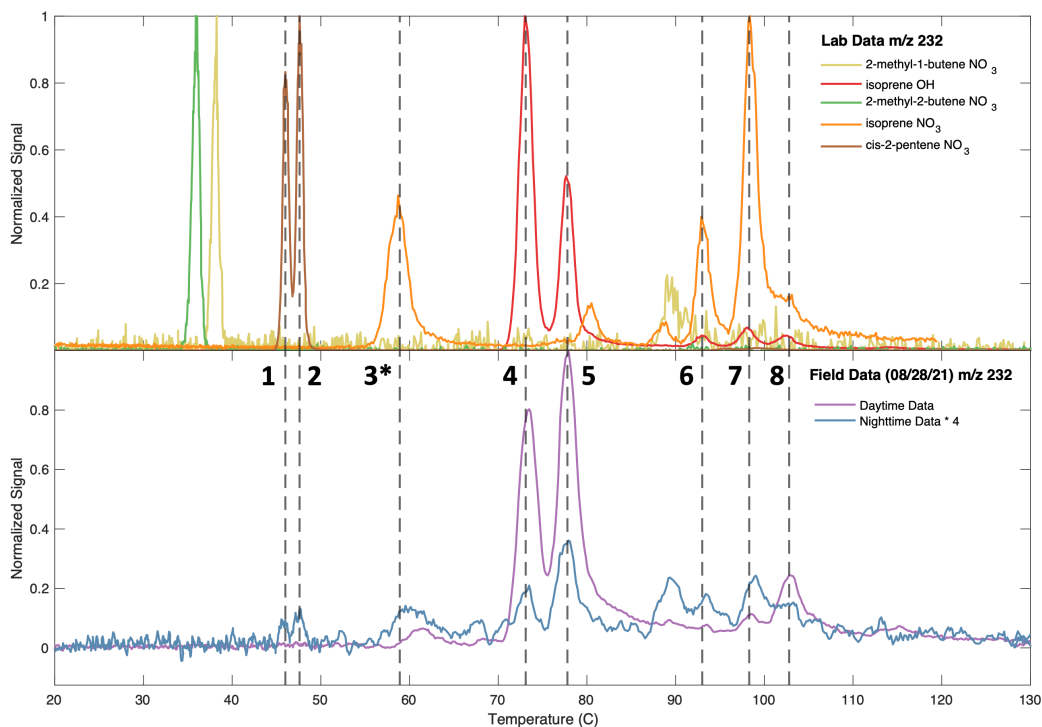


Figure 4.5: Ambient chromatographic data (lower panel) from 08/28/2021 with daytime signal in purple and nighttime data in blue. The nighttime signal is multiplied by a factor of 4 for clarity. Each trace in the lower panel is a sum of the traces during the daytime and nighttime period. Chromatographic data from a series of laboratory oxidation experiments (upper panel) are shown for comparison. Vertical dashed lines are drawn to align peaks in the laboratory and field data. The small shoulder of peak 3 eluting at $\sim 59^{\circ}\text{C}$ in the laboratory oxidation of isoprene has been tentatively assigned to the hydroxynitrate formed via OH addition at C3 (Teng, Crounse, and Wennberg, 2017).

While isoprene-derived hydroxy nitrates constitute the majority of the signal at m/z 232, other compounds (such as nitrooxy carbonyls derived from C5 alkenes) also appear at this mass. To confirm the identity of the observed compounds, elution temperatures were compared to those of the products observed in the dark and light oxidation experiments of 2-methyl-1-butene, isoprene, 2-methyl-2-butene, and cis-2-pentene. A list of assignments for the peaks shown in Figure 4.5, where assignments were possible, is given in Table 4.1. The cis-2-pentene-derived nitrooxy carbonyls that are assigned to peaks 1 and 2 are discussed in the section on anthropogenic nitrates.

The two major daytime peaks at this mass (peaks 4 and 5), which are identified using

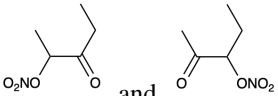
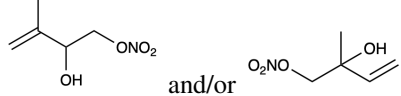
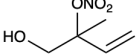
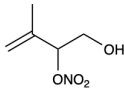
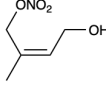
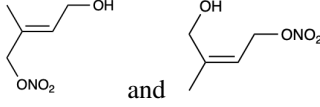
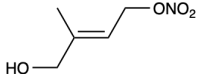
Peak	Elution Temperature (°C)	Assignment
1	46	
2	47.6	
3*	58.9	
4	73.1	
5	77.8	
6	93	
7	98.3	
8	102.8	

Table 4.1: Assignments of chromatographic peaks observed in ambient data at m/z 232. Peak numbers correspond to the peak numbers given in Figure 4.5. A star indicates that the peak appears to encompass two or more compounds.

the assignments from Teng et al (Teng, Crounse, and Wennberg, 2017), correspond to two β isomers (1-OH, 2-N and 4-OH, 3-N) of the isoprene-derived hydroxy nitrates (Table 4.1). During daytime, these nitrates are significantly more abundant than those of the δ -isomers, identified as peaks 6, 7, and 8. This is consistent with the observation that in the atmospheric OH-initiated oxidation of isoprene, the β -isomers constitute approximately 95% of the total isoprene-derived hydroxy peroxy radicals (Teng, Crounse, and Wennberg, 2017). The relative concentrations of these β isomers, however, are perturbed from the distribution observed in the laboratory. This is due, primarily, to the rapid hydrolysis of the 1-OH, 2-N isomer previously described by Vasquez et al. (Vasquez, Crounse, et al., 2020). Consistent with Vasquez et al., the ratio of 1-OH, 2-N to 4-OH, 3-N depends both on time of day (highest mid-day) and relative humidity (highest on dry days) (Figure C.8).

The nighttime signal at m/z 232 includes significant contributions from both β -

and δ -IHN. This is in keeping with previous observations that, in the NO_3 -initiated oxidation of isoprene under atmospheric conditions, the concentrations of β -nitrooxy and δ -nitrooxy peroxy radicals are approximately equal (Schwantes et al., 2015). The nitrooxy delta peroxy radicals are also much less likely to undergo autoxidation than their OH counterparts (Wennberg et al., 2018). Consistent with the NO_3 -initiated oxidation of isoprene in the laboratory, the formation of the δ -isomers (peaks 6, 7, and 8) and the 3-OH, 4N β isomer (peak 3*) of the hydroxy-peroxy radical are favored (Figure 4.5). While there is a small contribution to the overall nighttime signal at m/z 232 from the nitrooxy carbonyl formed in the oxidation of cis-2-pentene (peaks 1 and 2), throughout the daytime and nighttime the signal is (as expected) dominated by the products of NO_3 and, especially, OH-initiated isoprene oxidation.

Following the oxidation of isoprene, additional C4 hydroxy carbonyl nitrates are formed in the oxidation of the major isoprene oxidation products: methyl vinyl ketone (MVK), methacrolein (MACR), and the first generation IHN (Wennberg et al., 2018). The nitrates derived from these compounds are observed in our CIMS at m/z 234 and are discussed further alongside the alkene-derived hydroxy nitrates observed at this mass in the section discussing anthropogenic NCOCs.

Hydroxy Nitrates of Monoterpenes

Nitrates formed in the oxidation of monoterpenes are observed with CF_3O^- CIMS at m/z 300 and 316 (hydroxy and hydroperoxy nitrates, respectively). The diurnal profile of the signal at m/z 300 is consistent with compounds primarily formed in the evening (Figure 4.3), with an average maximum concentration of approximately 5 ppt before sunrise. Due to their high mass (and resulting poor separation) and the diversity of monoterpenes present in the Los Angeles atmosphere (Van Rooy et al., 2021), we are unable to determine the individual molecular contributions to this signal. However, it is clear from Figure 4.3 that, given the high reactivity of many of the monoterpenes (Ng et al., 2017), they represent a significant sink of NO_3 in the nighttime Los Angeles atmosphere.

Nitrooxy Carbonyls

Isoprene-derived nitrooxy carbonyls (mw 145) are observed in the CIMS at m/z 230. The diurnal profile of m/z 230 (Figure 4.3) is consistent with compounds primarily produced during the nighttime, supporting the hypothesis that the signal

at this mass originates from the NO_3 -initiated oxidation of isoprene. Consistent with this expectation, four isomers of the nitrooxy carbonyl produced in the laboratory NO_3 -initiated oxidation of isoprene, with identities assigned based on the work of Schwantes et al. (Schwantes et al., 2015) (Table 4.2), match the elution temperatures of compounds observed in the ambient data. However, in the ambient signal we observe a prominent fifth peak — at times carrying more than half of the m/z 230 signal — that is not produced in the NO_3 -initiated oxidation of isoprene in the laboratory (Figure 4.6).

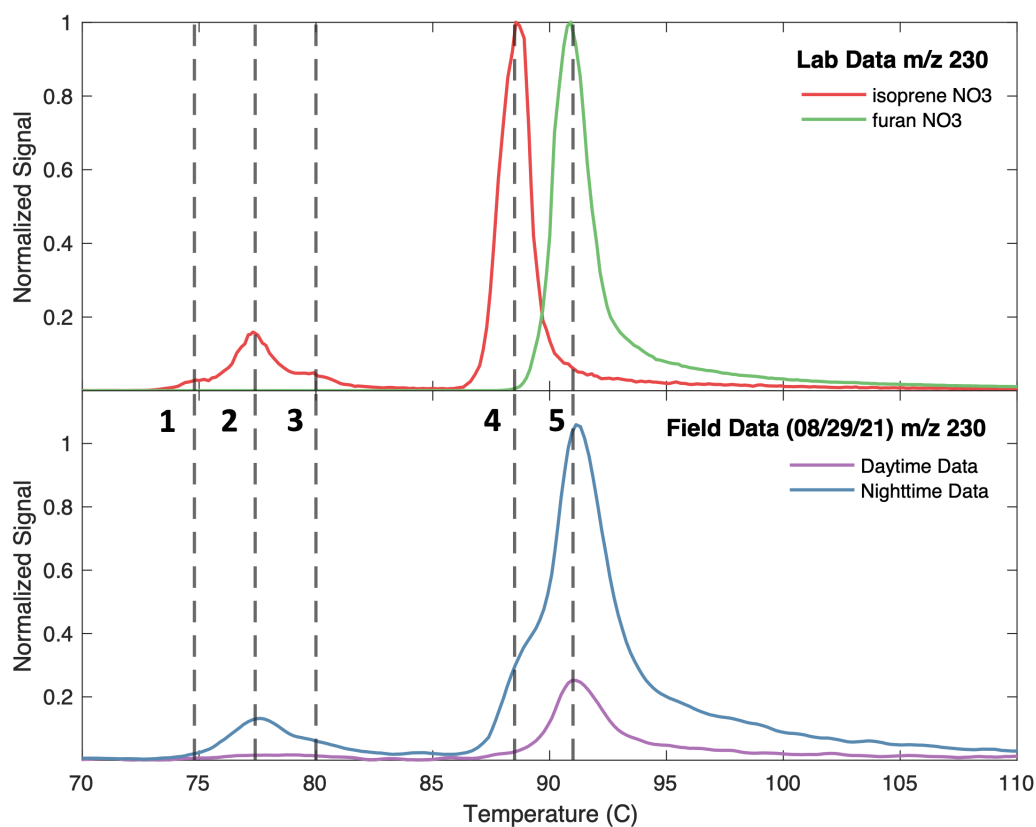


Figure 4.6: Sum of ambient chromatograms at m/z 230 taken during the daytime and nighttime (lower panel, purple and blue trace, respectively) on 08/29/2021. Chromatographic data at m/z 230 collected during the laboratory oxidations of furan and isoprene by NO_3 are shown in the upper panel for comparison. Vertical dashed lines are included to show alignments between peaks in the ambient and laboratory data.

This fifth peak persists throughout the daytime, while all four of the peaks corresponding to isoprene nitrooxy carbonyls are only present in significant concentra-

tions at night, consistent with the high OH reactivity of these compounds. The mass of the unique compound is shifted by -0.04 amu from the isoprene-derived nitrates. We identify the fifth peak as an organic nitrate compound produced in the NO_3 -initiated oxidation of furan (Figure 4.6). Additionally, in deuterium exchange experiments we observe no mass shift (Figure C.1), demonstrating that the compound contains no $-\text{OH}$ or $-\text{OOH}$ functional group. We therefore assign this peak to one of (or a sum of) the furan-derived nitrooxy carbonyl structures shown in Table 4.2. While it is impossible from this data alone to attribute a source to this compound, possible sources include the atmospheric NO_3 -initiated oxidation of furan (as was observed in the laboratory) or the NO_3 -initiated oxidation of butadiene. The exact mechanism of the formation of furan in the oxidation of butadiene is unclear, but has been observed in previous work (Tuazon et al., 1999). Both furan and butadiene were observed in the Los Angeles atmosphere during the summers of 2020 and 2022 in concentrations of approximately 10-20 ppt (Van Rooy et al., 2021). Considering the relative rates of the reactions of these compounds with NO_3 (the rate of the reaction of NO_3 with furan is an order of magnitude faster than that of butadiene), the low yields of furan observed in the reaction of butadiene, and the prominence of this peak in the ambient data, we expect that the oxidation of furan is a more likely source for this compound. This is further supported by laboratory work at Georgia Tech on the oxidation of 3-methylfuran by NO_3 , in which a $\text{C}_5\text{H}_5\text{NO}_5$ compound, likely a nitrooxy carbonyl, was observed to form in high yield (Joo et al., 2019). In the RECAP data, we also observe a signal at m/z 244 likely arising from a $\text{C}_5\text{H}_5\text{NO}_5$ nitrooxy carbonyl from the oxidation of methylfurans. The ratio of the signal at m/z 230 to m/z 244 is typically 4:1. The source of furans in Los Angeles is likely a combination of biomass burning and cooking. Clearly, furan chemistry contributed significantly to the gas-phase nitrate chemistry in Pasadena in the summer of 2021 and the formation and loss of these compounds should be further investigated.

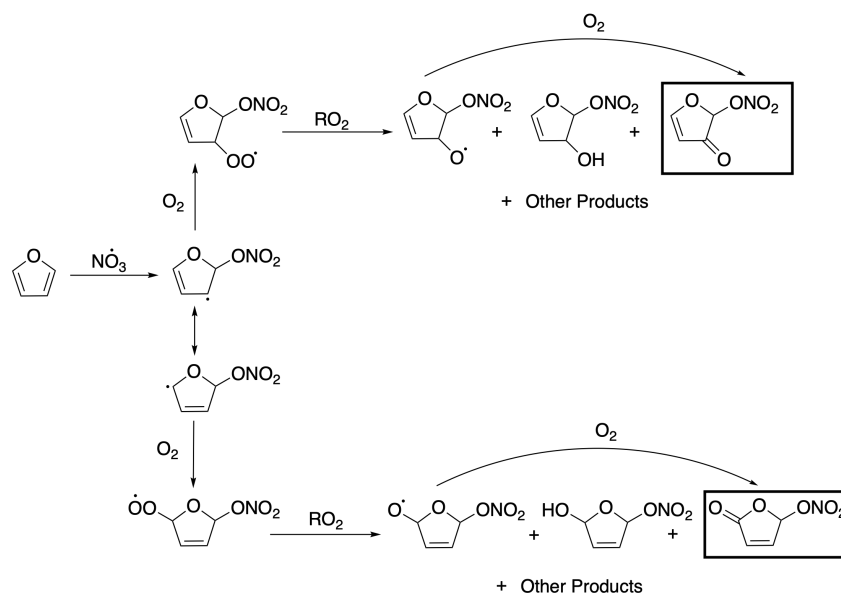


Figure 4.7: Possible mechanism for the formation of the carbonyl compound observed at m/z 230 via oxidation of furan by NO_3 .

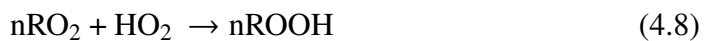
Peak	Elution Temperature (°C)	Assignment
1	74.5	
2	77.3	
3	80.1	
4	88.7	
5	91.3	

Table 4.2: Assignments of chromatographic peaks observed in the ambient data at m/z 230. Peak numbers correspond to those peak numbers given in Figure 4.6.

While the formation of nitrooxy carbonyls in the nighttime oxidation of monoterpenes is also theoretically possible, little to no signal at the mass of these compounds (m/z 298) is observed in the ambient data. This is likely due to the fact that the majority of the monoterpene-derived peroxy radicals generated at night are tertiary peroxy radicals that cannot form the carbonyl (Hallquist et al., 1999) or that these peroxy radicals preferentially undergo autoxidation (Berndt, Richters, Jokinen, et al., 2016; Ng et al., 2017; Nah et al., 2016).

Nitrooxy Hydroperoxides

The nitrooxy hydroperoxides of isoprene, formed in the reaction of isoprene-derived $n\text{RO}_2$ with HO_2 (Reaction 4.8), are observed at m/z 248.



To identify these compounds, we compare the elution temperatures of the ambient peaks at this mass to those formed in the dark oxidation of isoprene (Figure C.4). At night, two of the major peaks observed in the ambient data have the same elution temperatures as the two nitrooxy hydroperoxides produced in NO_3 -initiated oxidation of isoprene. However, several additional compounds are also observed at this mass, including compounds formed in the oxidation of C_6 alkenes (e.g., 2-methyl-2-pentene and n -hexenes) or hydroxynitrates produced via oxidation and subsequent H-shift chemistry of hexane. The overall concentration of compounds at this mass is approximately equal to the concentration of isoprene-derived hydroxy nitrates at night observed throughout the campaign (Figure C.7), suggesting that the reaction of $n\text{RO}_2$ with HO_2 may play an important role in this region at night.

Anthropogenic Nitrates

Small Alkene-Derived Hydroxy Nitrates

Hydroxy nitrates derived from alkenes are formed both in the daytime by OH oxidation and at night by NO_3 oxidation. In our CIMS the smallest of these hydroxy nitrates, the ethene-derived hydroxy nitrate, is observed at m/z 192. The larger alkene-derived hydroxy nitrates are then observed at $m/z = 192 + (n \times 14)$, where n is the number of additional CH_2 groups. For hydroxy nitrates derived from C_4 and C_5 alkenes, the products of multiple precursor alkenes contribute to the signal at the corresponding m/z . These products were separated in the GC-CIMS, and were identified by comparison to the elution temperatures of hydroxy nitrates formed in the laboratory oxidation of various alkenes. Those compounds that we identified

in the ambient data are given in Table 4.3, and the behavior of these individual compounds are discussed below.

The diurnal profiles of these small alkene-derived hydroxy nitrates are consistent with their formation primarily during the daytime (for example, Figure 4.3a, b, and e). Further, the signals at the masses of these hydroxy nitrates in the CToF-CIMS are well-correlated, consistent with a common source for the precursors of these compounds (Figure 4.8).

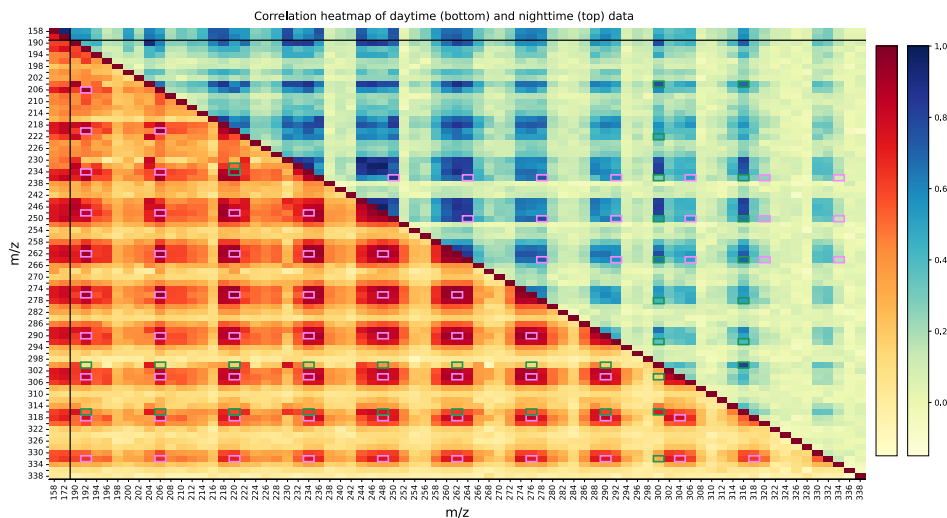


Figure 4.8: Correlation matrix for all even masses between m/z 190 and m/z 338. m/z 158 and m/z 172 are also included as the first two rows and separated from the other m/z by solid black lines. The lower left triangle shows correlations during the daytime (warm colors) and the upper right triangle shows correlations during the nighttime (cool colors). Pink boxes highlight correlations between masses in the m/z 192 + 14n series. Green boxes highlight correlations between masses that contain biogenic nitrates. Here, ‘daytime’ is defined as 8:00 AM – 5:00 PM and ‘nighttime’ is defined as 8:00 PM – 4:00 AM. Figure courtesy of Haroula Baliaka.

The relative production rates of a set of isomeric hydroxy nitrates during the daytime can be estimated by taking the sum of the products of the observed concentrations of the parent alkenes (Van Rooy et al., 2021), their rate constants with OH, and the nitrate yields from Reaction 4.4a. Figure 4.9 shows that the relative signals at the masses of these small alkene-derived hydroxy nitrates are generally consistent with this estimate of their relative production rates. The composition of the signal at each mass, however, consists of a diversity of compounds, and therefore a detailed picture of the overall chemistry requires chromatographic separation.

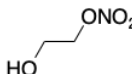
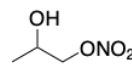
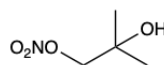
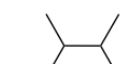
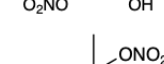
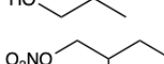
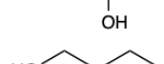
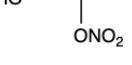
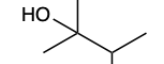
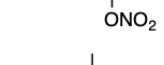
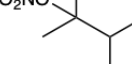
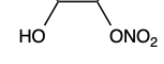
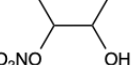
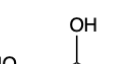
m/z	Elution Temperature (°C)	Assignment
192	48.1	
206	46.8	
	52.0	
220	45.5	
	52.6	
	58.1	
	65.0	
	72.9	
234	49.8	
	61.3	
	64.4	
	69.1	
	72.1	
	82.1	
	87.5	
	90.2	
	100.3	

Table 4.3: Assignments of ambient chromatographic peaks at masses that correspond to hydroxy nitrates primarily derived from small alkenes.

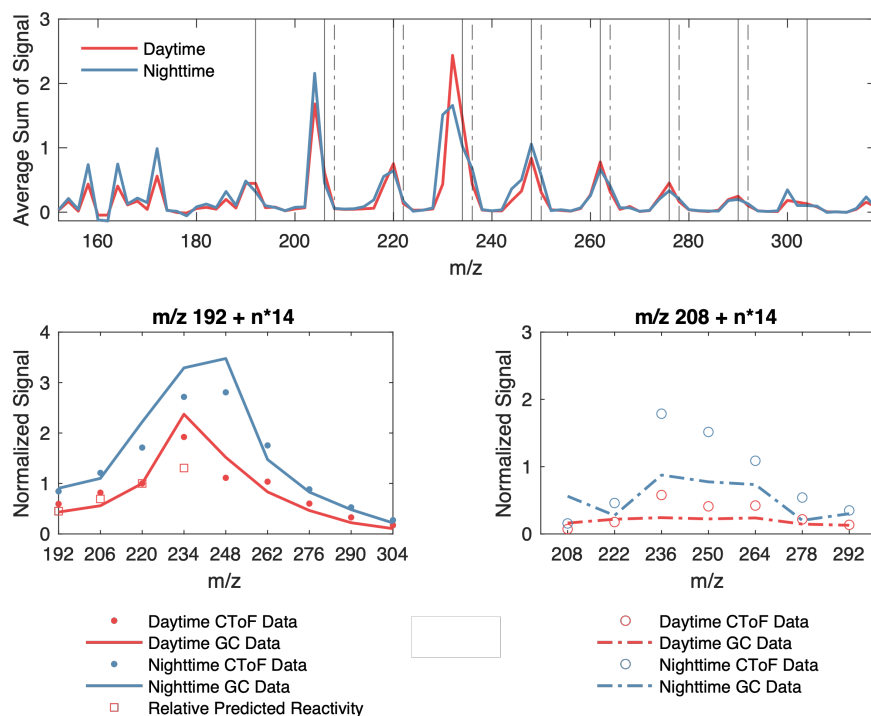


Figure 4.9: Comparison of the average relative sums of the normalized signals over the time period between August 28th, 2021 and September 5th, 2021 for the GC-HRToF (lines) and CToF-CIMS (circles) at each of the small alkene-derived hydroxy nitrate masses (lower left panel) and the small alkene-derived nitrooxy hydroperoxide masses (lower right panel) during both the daytime (red) and the nighttime (blue). Signals are given relative to the sum of the signal at the m/z 220. The open squares in the lower left panel show the relative predicted reactivities, calculated as described in the text. Note that the discrepancy in the average sum of the signal across the CToF and GCToF in the hydroxyperoxide series is due to low transmission of these compounds in the 2m GC, as observed in Chapter 3. The upper panel shows the average sum of the CToF-CIMS signal at all masses between m/z 152 and m/z 318 during the daytime (red) and nighttime (blue) between August 28th, 2021 and September 5th, 2021. Solid vertical lines denote masses in the hydroxy nitrate series (m/z 192 + $n \cdot 14$) and dashed vertical lines denote the masses in the hydroxy hydroperoxide series (m/z 208 + $n \cdot 14$).

The reactions of ethene and propene with OH and NO₃ produce one isomer of a C₂ hydroxy nitrate at m/z 192 and two isomers of a C₃ hydroxy nitrate at m/z 206, respectively. The compounds observed at these masses in the ambient data have elution temperatures consistent with these hydroxy nitrates as observed in laboratory

oxidation data (Figures C.2 and C.3), with little to no contribution from compounds eluting at different temperatures. Therefore, we assign the entirety of the signal at m/z 192 to the ethene-derived hydroxy nitrate, and similarly that of m/z 206 is assigned to the propene-derived hydroxy nitrate. At m/z 206, the structural isomers of the propene-derived hydroxy nitrate are well separated and, as expected, the relative abundance of these isomers changes significantly as the dominant oxidant changes from OH during the daytime to NO_3 at night (both OH and NO_3 favor addition at the terminal carbon). In total, the nitrates produced from these two alkenes contribute (on average) a maximum of 7% to the total overall signal at even masses during the daytime and 3% at night.

The chromatographic signal at m/z 220, the mass consistent with hydroxy nitrates derived from C4 alkenes, is more complex (Figure 4.10). Laboratory oxidation experiments in the presence of OH/NO and/or NO_3 with 2-methylpropene, cis-2-butene, 1-butene, and butadiene as precursors were performed for comparison to the ambient data. Throughout the campaign, major contributions to this signal were consistent with hydroxynitrates produced from methylpropene and 1-butene during the daytime, with a more minor contribution from cis-2-butene-derived hydroxy nitrates. This is largely consistent with the relative emissions, rate constants, and nitrate yields of these three compounds with respect to reaction with OH. During the daytime, an additional prominent peak is observed at an elution temperature matching that of a nitrate formed in the oxidation of butadiene, along with another nitrate that elutes at approximately 90°C (Figure 4.10). The precise identities of these nitrates are uncertain.

During the nighttime, the contribution to the overall signal at m/z 220 is more evenly distributed across the various C4 hydroxy nitrate isomers. Although the tertiary hydroxy nitrate isomer of methylpropene (assigned to the peak eluting at approximately 45.5°C) appears to be formed during the night, other compounds exhibit a diurnal behavior more consistent with formation during the daytime and persistence at night. This observation is consistent with the much higher predicted nighttime production rate of methylpropene-derived nitrates as compared to other C4 alkenes. However, similarly to the daytime signal, there is a distinct compound observed at an elution temperature (87.6°C) inconsistent with those of the hydroxy nitrates of the alkenes and with the butadiene-derived nitrates observed during the daytime. The elution temperature is consistent with a compound formed in the oxidation of 2-methylpropene that is not one of the hydroxy nitrates, but this compound

remains unidentified. Overall, the signal at m/z 220 peaks at approximately noon at a concentration of 15 ppt, decreasing throughout the day to an average concentration of approximately 7 ppt at night. This corresponds to, on average, a maximum of 5% of the total signal at even masses during the daytime and a maximum of 3% of the total signal at even masses during the night. Despite the contributions to the signal from unidentified peaks, the production rate estimated from the alkenes relative to ethene matches their signal relative to ethene, suggesting that it is possible that these additional compounds are formed in the oxidation of C4 alkenes.

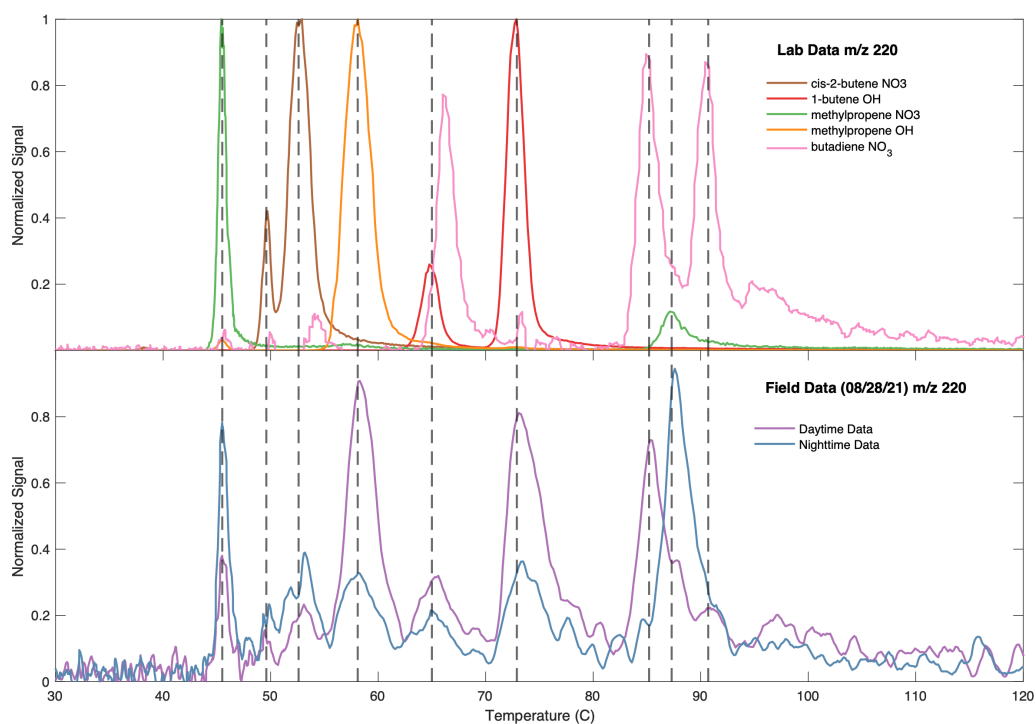


Figure 4.10: Ambient chromatographic data at m/z 220 (lower panel) from 08/28/2021 with daytime signal in purple and nighttime data in blue. Each trace in the lower panel is a sum of the traces during the daytime and nighttime period. Chromatographic data from a series of laboratory oxidation experiments (upper panel) are shown for comparison. Vertical dashed lines are included to demonstrate alignment between the elution temperatures of laboratory and ambient peaks.

Hydroxy nitrates formed in the oxidation of C5 alkenes are observed at m/z 234. As mentioned previously, MVK and MACR-derived hydroxy nitrates, formed in the oxidation of isoprene, are also observed at this mass, as are compounds formed in the oxidation of pentane by OH and subsequent hydrogen shifts. Laboratory

oxidation experiments of 2-methyl-1-butene, 2-methyl-2-butene, 1-pentene, cis-2-pentene, pentane, and isoprene were performed for comparison to the ambient data (Figure 4.11). The proposed identities of the compounds observed in the ambient data at this mass are given in Table 4.3. MVK- and MACR-derived hydroxy nitrates, identified as contributing to the prominent peaks eluting at 90.2°C and 100.3°C, are observed during the daytime. By integrating both the total daytime and nighttime GC signals at m/z 234 and the individual peaks at 90.2°C and 100.3°C, we find that MVK- and MACR-derived nitrates contribute on average approximately 49($\pm$ 12)% of the total signal at m/z 234 during the daytime and 21($\pm$ 8)% to the total signal at m/z 234 at night (Table C.7). Especially in the case of the compound eluting at 100.3°C (identified as the MACR-derived nitrate), the peak shapes at 90.2°C and 100.3°C suggest that small concentrations of additional compounds may also contribute to the signal at these elution temperatures. Additionally, there is significant production of the hydroxy nitrates derived from 2-methyl-1-butene, cis-2-pentene, and 1-pentene, with a small contribution to the signal from the hydroxy nitrates derived from 2-methyl-2-butene. Although not shown in the figure for simplicity, the hydroxy nitrates formed at m/z 234 in the OH-initiated oxidation of pentane elute at temperatures quite close to those produced in the oxidation of 1-pentene and MVK at 87.5°C and 90.2°C, respectively. Therefore, there is likely some contribution from the pentane OH products to the peaks observed at these elution temperatures in the ambient data. An additional unknown compound elutes during the daytime at approximately 78.8°C, inconsistent with the elution temperatures of compounds in any of the above oxidation experiments, but this contribution is relatively minor. At night, the concentration of the MVK- and MACR-derived nitrates significantly decreases. Several of the alkene-derived hydroxy nitrates appear to either undergo secondary reaction or persist throughout the night, while there seems to be more significant nighttime production of the hydroxy nitrate derived from 2-methyl-1-butene.

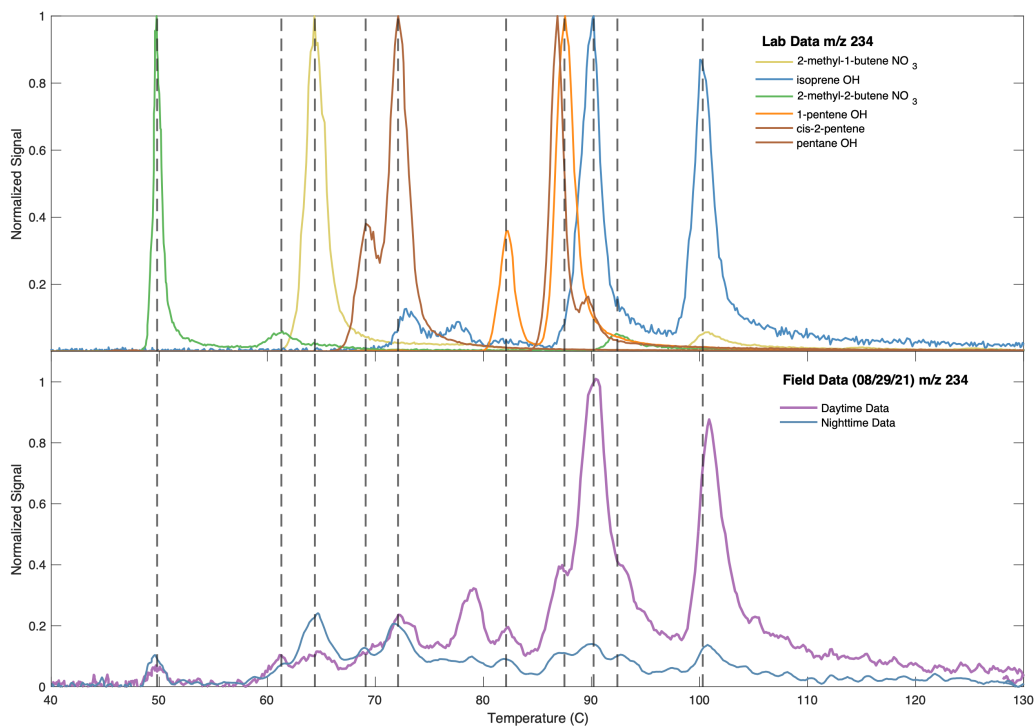


Figure 4.11: Ambient chromatographic data at m/z 234 (lower panel) from 08/29/2021 with daytime signal in purple and nighttime data in blue. Each trace in the lower panel is a sum of the traces during the daytime and nighttime period. Chromatographic data from a series of laboratory oxidation experiments (upper panel) are shown for comparison.

The overall signal at m/z 234 peaks at around noon at a concentration of approximately 25 ppt on average, decreasing throughout the day to a concentration of approximately 5 ppt at night. This corresponds to a maximum average contribution of 10% to the total signal at even m/z during the daytime and approximately 3% to the total signal at even m/z at night. This diurnal behavior is largely driven by the formation of MVK and MACR-derived hydroxy nitrates, accounting for the discrepancy between the predicted relative formation rate and relative signal observed in Figure 4.9. However, despite the importance of MVK and MACR-derived nitrates at m/z 234, there is still significant formation of hydroxy nitrates via the reaction of several small C5 alkenes, as can be seen in Figure 4.11.

Nitrooxy Carbonyls

Nitrooxy carbonyls are formed primarily in the self reaction of nRO_2 or in the oxidation of hydroxy nitrates via abstraction of the hydrogen atom α to the $-\text{OH}$ group. These carbonyls appear at an m/z two less than that of the corresponding hydroxy nitrates. Table 4.4 gives the structures of the identified nitrooxy carbonyls formed in the oxidation of C2-C5 alkenes, which begin at m/z 190 and increase by 14 with each addition of a CH_2 group.

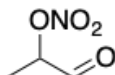
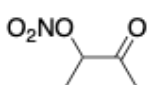
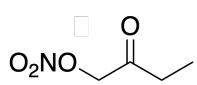
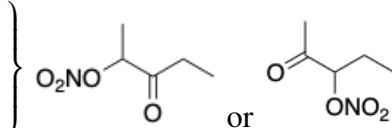
m/z	Elution Temperature ($^{\circ}\text{C}$)	Assignment
204	41.9	
218	38.2	
	54.3	
232	45.9	
	47.5	

Table 4.4: Assignments for ambient peaks corresponding to nitrooxy carbonyls derived from small alkenes in the GC-CIMS. Note that where there are multiple isomers, assignments are speculative.

No significant signal at the mass of the ethene-derived nitrooxy carbonyl (m/z 190) was observed in the ambient data. However, a prominent peak at the mass of a C3 nitrooxy carbonyl (m/z 204) is observed in the ambient data at an elution temperature of 41.9°C . C3 nitrooxy carbonyls are formed both in the NO_3 -initiated oxidation of propene and the NO_3 -initiated oxidation of isoprene. The identity of the compound observed in the ambient data is assigned by comparison to the chromatograms of this mass observed in the NO_3 -initiated dark oxidation of propene. While there are two peaks at m/z 204 which appear in the dark oxidation of propene, one of which matches the elution temperature of the prominent ambient peak at this mass and one of which matches the elution temperature of a more minor peak in the ambient data, only the more prominent peak is assigned to a C3 nitrooxy carbonyl (Table 4.4). These peaks appear to be the only contribution to the signal at m/z 204.

The ambient GC signal at m/z 218, the mass of C4 nitrooxy carbonyls in the CIMS, contains several prominent compounds present during both the daytime and the nighttime. Two of these compounds elute at temperatures corresponding to those of nitrooxy carbonyls formed in the NO_3 -initiated oxidation of *cis*-2-butene (38.2 °C) and 1-butene (54.3 °C) and are assigned to these C4 nitrooxy carbonyls (Table 4.4). However, several of the compounds observed at m/z 218 in the ambient data exhibit diurnal behavior consistent with a unique daytime source, and are therefore likely not nitrooxy carbonyls. Two peaks observed in the ambient data, for example, correspond to the hydroxy nitrates formed in the oxidation of butadiene, with elution temperatures of 66.3 °C and 90.4 °C. However, the GC signal at m/z 218 is complex and several compounds, primarily a prominent peak at 58.7 °C, remain unidentified.

The overwhelming majority of the signal at m/z 232, the mass at which C5 alkene-derived nitrooxy carbonyls are observed, is composed of isoprene-derived hydroxy nitrates, as discussed in the previous section on biogenic nitrates. However, two small peaks observed in the nighttime ambient data at this mass elute at a temperature matching those of the nitrooxy carbonyls formed in the laboratory NO_3 -initiated oxidation of *cis*-2-pentene (45.9°C and 47.5°C), and these ambient peaks are thus assigned to the two isomers of this nitrooxy carbonyl.

As described above, several small alkene-derived nitrooxy carbonyls are observed in this study (Table 4.4) and these compounds play a prominent role in the nitrate chemistry observed in the ambient atmosphere during the campaign.

Nitrooxy Hydroperoxides

Small alkene-derived nitrooxy hydroperoxides are observed in the GC-CIMS at $m/z = 208 + n \times 14$, where $m/z = 208$ is the mass of the ethene-derive nitrooxy hydroperoxide and n is the number of additional CH_2 groups for each subsequent compound in the series. These hydroperoxides are produced at night in the reaction of nitrooxy peroxy radicals with HO_2 (when NO levels are effectively zero due to titration by O_3). Figure 4.9 shows that, while the formation of these compounds is less significant in the oxidation of C2 and C3 alkenes, their production appears to be more important in the oxidation of C4, C5, and C6 compounds, reflecting the higher NO_3 reactivity of some of these compounds. Consistent with the observation that the signal at these masses is low for ethene- and propene-derived $n\text{RO}_2$, no clear peaks are observed at m/z 208. At m/z 222, we observe one primary peak that is present exclusively at night. This peak has an elution temperature consistent with

the nitrooxy hydroperoxide formed in the laboratory oxidation of propene by NO_3 , and is therefore assigned as such. The presence of only one peak suggests either that only the major addition of NO_3 to form a secondary nRO_2 is occurring at a significant rate or that the isomers of this compound are poorly separated. Due to the excellent separation of the hydroxy nitrate isomers observed at m/z 206, this latter possibility seems unlikely. We therefore assign the peak at m/z 220 to only one isomer, likely that corresponding to the more abundant nighttime nRO_2 .

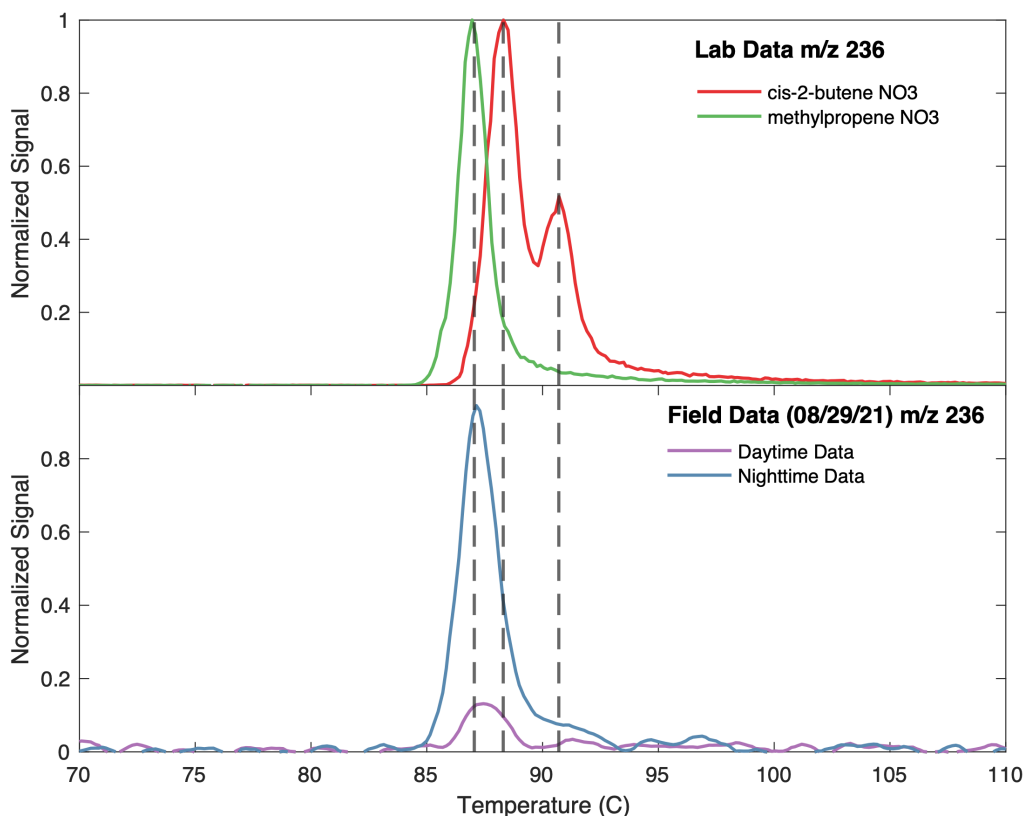


Figure 4.12: Ambient chromatographic data at m/z 236 (lower panel) from 08/29/2021 with daytime signal in purple and nighttime data in blue. Each trace in the lower panel is a sum of the traces during the daytime and nighttime period. Chromatographic data from a series of laboratory oxidation experiments (upper panel) are shown for comparison.

At m/z 236, the mass of the C4 alkene-derived nitrooxy hydroperoxide, we observe one primary peak in the ambient data eluting at 87.1°C. The identity of this compound is assigned to the methylpropene-derived nitrooxy hydroperoxide by comparison to our laboratory oxidation experiments (Figure 4.12). There is a small

shoulder at higher temperature and a second peak at $\sim 91^\circ\text{C}$ that is suggestive of a small amount of nitrooxy hydroperoxides produced from the 2-butenes. Using the ratio of the abundance of 2-butenes and methylpropene from Van Rooy et al. (Van Rooy et al., 2021) we calculate that the NO_3 reactivity with the cis- and trans-2-butenes are about 20% of the reactivity with methylpropene. The prominence of methylpropene-derived nighttime nRO_2 chemistry in this case is consistent with several other observations of significant contributions of methylpropene-derived nitrates in this study — this general prominence of nighttime methylpropene chemistry is due to a combination of its much higher abundance and as fast, if not faster, reactivity compared to other C4 alkenes.

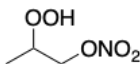
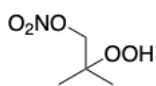
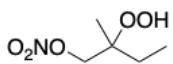
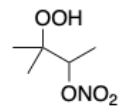
m/z	Elution Temperature	Assignment
222	85.0	
236	87.1	
250	92.0	
	100.2	

Table 4.5: Assignments for peaks corresponding to nitrooxy hydroperoxides derived from small alkenes in the GC-CIMS. Note that where multiple isomers are possible the assignments are speculative.

Finally, three peaks are observed in the ambient chromatographic data at m/z 250, the mass corresponding to C5 nitrooxy hydroperoxides. Two of these peaks are significantly more prominent than the third (Figure 4.13). By comparison to the elution temperatures of nitrooxy hydroperoxides formed in the laboratory oxidation of 2-methyl-2-butene and 2-methyl-1-butene, we assign these peaks to the nitrooxy hydroperoxides derived from these compounds (Table 4.5). The identity of the third peak is currently unknown. However, the high concentrations of the 2-methyl-2-butene and 2-methyl-1-butene-derived nitrooxy hydroperoxides suggest that the nRO_2 of these precursor alkenes undergo significant reaction with HO_2 at night throughout the campaign.

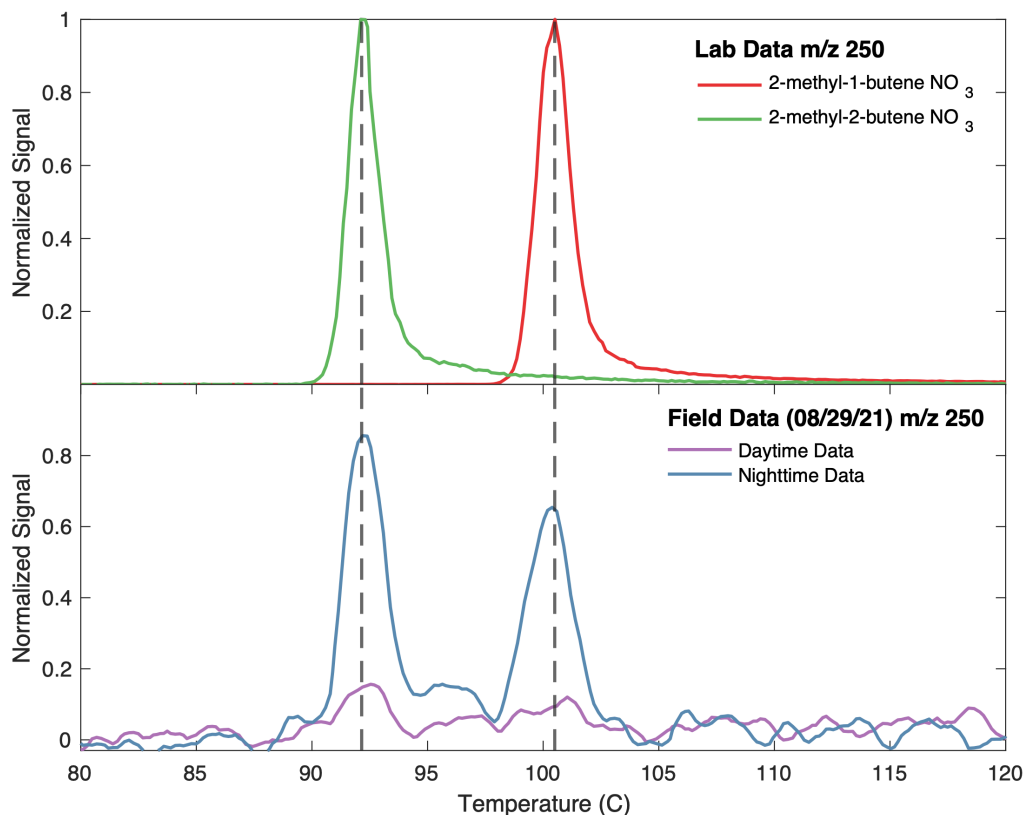


Figure 4.13: Ambient chromatographic data at m/z 250 (lower panel) from 08/29/2021 with daytime signal in purple and nighttime data in blue. Each trace in the lower panel is a sum of the traces during the daytime and nighttime period. Chromatographic data from a series of laboratory oxidation experiments (upper panel) are shown for comparison.

Nitroaromatics

A significant contribution to the total nitrogen-containing organic compounds is observed at the mass corresponding to nitroaromatics. Nitroaromatics are primarily formed in the atmospheric oxidation of benzene and other aromatic compounds such as toluene and catechol in the presence of NO_2 . These nitroaromatics generally undergo a fluorine transfer reaction in our GC-CIMS and thus are observed at $m/z = m_w + 19$. For example, nitrophenol, which has a molecular weight of 139, is observed at m/z 158. The formation of these nitroaromatic compounds has been shown to play a significant role in urban chemistry in other areas with high NO_x and significant anthropogenic VOC emissions (Wang et al., 2019). In our data, a signal at m/z 158 is observed in both the GC-CIMS and in the CToF-CIMS equal to the

signal observed at m/z 220 during the time period discussed here (Figure C.6). The identity of the ambient chromatographic peak observed at m/z 158 was confirmed by comparison of the chromatography to that of a 2-nitrophenol standard present in the hot calibration system of the GC-CIMS. The signal at m/z 172, corresponding to addition of OH and NO₂ to toluene, is of similar magnitude. The sum of the signal at m/z 158 and m/z 172 contributes up to 10% of the total signal at even m/z observed on average. Therefore, along with small alkene-derived chemistry, nitroaromatic compounds make a significant contribution to the anthropogenic nitrate chemistry observed during the campaign.

4.4 Conclusion

The census of multifunctional organic nitrates observed during the RECAP-CA field campaign in Pasadena in the summer of 2021 provides a measure of which VOCs contribute to the formation of ozone and organic aerosol. Biogenic (largely isoprene-derived) and anthropogenic hydrocarbons play similar roles in the overall organic nitrate chemistry during the time period examined here, with significant contributions to the anthropogenic nitrate budget from both small alkenes and aromatic compounds such as benzene and toluene. Furan-derived nitrooxy carbonyls are a major nighttime reservoir of organic nitrogen. Further, the small alkene-derived nitrates are wellcorrelated with each other, consistent with a common source. The ratio of the measured concentrations of these nitrates are well-predicted by their production rates estimated from previous measurements of the ratios of the concentrations of the parent alkenes.

Chapter 5

CONCLUSIONS AND OUTLOOK

5.1 Conclusions and Summary

In this thesis, I have examined the bimolecular reactions of organic peroxy radicals in both low NO and high NO environments. This work has addressed several gaps in the literature regarding the rates and products of these reactions for a variety of alkene-derived peroxy radicals in both regimes in the laboratory and in the ambient environment.

In Chapters 2 and 3, I presented laboratory chamber work aimed at identifying the products formed in the self- and cross-reactions of RO₂, reactions which can be important in low NO environments. With these results I demonstrated, using GC-CIMS and comparison to synthesized standards, that the accretion product (ROOR) is formed at appreciable rates in small alkene-derived peroxy radical systems (with branching fractions up to 23%), challenging prior assumptions regarding the relative importance of this reaction pathway. These results suggest that the formation of these ROOR should likely be considered in models of atmospheric peroxy radical chemistry, especially in regions with low NO concentrations.

To further understand the role of ROOR formation in low NO regimes, a relationship between ROOR formation and peroxy radical structure is required. In Chapter 3, I showed that ROOR formation rates ($k_{\text{RO}_2+\text{RO}_2} \alpha_{\text{ROOR}}$) for peroxy radical self-reactions are largely similar for C2-C4 alkene-derived RO₂ with the same level of substitution, with little-to-no dependence on carbon number. However, these rates differ significantly across tertiary, secondary, and primary peroxy radicals, with $k_{\text{RO}_2+\text{RO}_2} \alpha_{\text{ROOR}}$ decreasing by approximately an order of magnitude with each increasing level of substitution. Despite low ROOR formation rates for tertiary peroxy radicals, I also demonstrated that $k_{\text{RO}_2+\text{RO}_2} \alpha_{\text{ROOR}}$ values for cross-reactions between tertiary RO₂ and less substituted RO₂ can be significant, suggesting that although the self-reactions of tertiary peroxy radicals may not be a significant source of ROOR, their cross reactions may play a more important role in ROOR formation. A mathematical relationship between the self-reaction rates of individual RO₂ and their respective cross-reaction rates with other RO₂ facilitates prediction of this phenomenon for a wider suite of peroxy radicals than that studied here. Prior

studies have suggested that the cross-reaction rate of two peroxy radicals can be estimated by taking the geometric mean of their respective self-reaction rates. In Chapter 3, I suggest that the arithmetic mean equally captures this relationship, both for the overall rate constants of these reactions and for $k_{\text{RO}_2+\text{RO}_2} \propto \alpha_{\text{ROOR}}$.

Although NO concentrations have continued to decrease with increasing regulations in some regions, high NO concentrations continue to influence tropospheric chemistry in many urban areas, including Los Angeles. In Chapter 4, I presented ambient observations of the formation of nitrogen-containing organic compounds (NCOCs) during the summer of 2021 and identified those compounds that played a major role in the urban atmosphere in Los Angeles during this time period. As part of the RECAP-CA campaign, I and others in our laboratory observed significant contributions to the formation of NCOCs from the oxidation of both anthropogenic and biogenic sources, and performed speciated measurements of these organic nitrates. We showed that the relative contributions of small alkene-derived nitrates during the daytime can be well-estimated by their relative production rates and that the signals corresponding to these compounds are well-correlated, indicating that they have similar sources. At night, reactions between nRO_2 and HO_2 , in addition to the formation of hydroxy nitrates and nitrooxy carbonyls, were observed to play an important role in organic nitrate formation. We further demonstrated that organic nitrogen compounds derived from furan and aromatic compounds played a surprisingly important role in the organic nitrogen budget and should be considered in future studies of urban organic nitrogen chemistry.

5.2 Future Work

Studies of ROOR Formation

Although Chapters 2 and 3 comprise a systematic study of the relationship between structure and ROOR formation, further work is needed to more completely probe this relationship. Studies examining the oxidation of longer-chain alkenes under high RO_2 conditions, for example, would provide more insight into the relationship between ROOR formation and peroxy radical size. In Chapters 2 and 3 I presented measurements of $k_{\text{RO}_2+\text{RO}_2} \propto \alpha_{\text{ROOR}}$ for C2-C4 alkenes, and the methods described within could be used to measure these values (or α_{ROOR} values directly, as in Chapter 2) for C5 and C6 alkenes, including pentenes, hexenes, branched butenes, and branched pentenes. Further, the work discussed here largely focused on the self- and cross-reactions of branched and straight-chain alkenes, and additional studies of ROOR formation should be conducted for alkenes with differing structures, such

as cycloalkenes. Preliminary work examining the oxidation of cyclopentene using the methods described in Chapters 2 and 3 did not observe the formation of ROOR, in contrast to studies that have observed rapid ROOR formation in the oxidation of aromatic hydrocarbons such as α -pinene and 1,3,5-trimethylbenzene (Berndt, Mentler, et al., 2018; Molteni et al., 2019; Bates, Burke, et al., 2022; Berndt, Scholz, et al., 2018). Clearly, the formation of ROOR in aromatic and cycloalkene oxidation systems requires further study, and such studies would improve the general understanding of the relationship between RO₂ structure and accretion product formation.

The ultimate fate of ROOR in the atmosphere also requires further study. Accretion products, especially for larger parent hydrocarbons, usually have low volatilities and thus have the potential to partition to secondary organic aerosol (SOA) and contribute to subsequent particle growth. As discussed in Chapter 1, recent work in both the laboratory and the field has confirmed that these compounds potentially play a role in particle formation and/or growth (B. H. Lee, Lopez-Hilfiker, et al., 2018; Bates, Burke, et al., 2022). However, there have been no laboratory studies aimed directly at probing the aerosol formation potential of these compounds and their importance in aerosol formation in a variety of potential chemical environments, including those that might mimic ambient environments. Further, although the photolysis rate of the ethene-derived ROOR was measured in Chapter 2, the photolysis rates and OH reaction rates of a wider variety of ROOR compounds (where possible) should be studied to determine the lifetime of these compounds in the atmosphere with respect to a variety of loss processes.

Studies of Dimerization Chemistry

As discussed in Chapters 2 and 3, additional dimer products have been observed in both the particle and the gas-phase, including the formation of dimer esters. The formation of these compounds have been observed in the O₃ + OH oxidation of β -pinene (Kenseth et al., 2018) and in the ozonolysis of α -pinene (Peräkylä et al., 2023). In the latter study, dimer esters are proposed to form in the self- and cross-reactions of RO₂ via alkoxy scission in the intermediate complex. However, masses corresponding to these ester products were not observed in the oxidation systems examined in Chapters 2 and 3. It is likely that peroxy radical structure plays an important role in the competition between the formation of these various possible dimer products. Therefore, alongside further study of the formation of ROOR in the RO₂ self-reaction, product studies for a variety of peroxy radicals should

be performed to determine the relative importance of these various dimerization mechanisms. The development of structure-activity relationships for these accretion mechanisms, for comparison to structure-activity relationships for ROOR formation, would be ideal for predicting the potential importance of each of these accretion mechanisms in the real atmosphere.

Measurements of Speciated NCOCs

While Chapter 4 contains a comprehensive catalogue of speciated organic nitrates in the ambient atmosphere in Los Angeles during the summer of 2021, a limited number of peaks at several masses, most notably at m/z 220 and m/z 234, remain unidentified. High resolution analyses of these signals and subsequent laboratory investigations should be performed to identify some of these compounds. Additionally, this work focused exclusively on examining the results from even masses, which encompass NCOCs in our CIMS – several compounds present at odd m/z (likely functionalized organic compounds without nitrogen) also have complicated chromatographic signals in the GC-CIMS and require further study and identification. Significant insight into local organic peroxy radical chemistry can likely be gained through further study of the compounds present at these odd m/z .

As discussed in Chapter 4, significant concentrations of furan-derived nitrates were observed throughout the time period examined here. Further work should be conducted to determine the source of these furan-derived nitrates, and measurements should be conducted in other regions to determine if these or other furan-derived compounds play an important role in other urban environments. Additionally, subsequent measurements should be conducted over a range of time periods in Los Angeles to determine how the contribution of these furan-derived nitrates varies on a longer temporal scale.

Finally, the techniques used in Chapter 4 for measurements of speciated NCOCs should be used to expand the measurements of these compounds to a wider variety of regions and environments. As discussed in Chapter 1 and Chapter 4, comprehensive measurements of individual NCOCs are rare but important for a complete picture of tropospheric chemistry in a region. The results of Chapter 4 demonstrate the rich information available from these measurements and the value they pose in elucidating local chemistry.

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Appendix A

SUPPLEMENTARY INFORMATION FOR CHAPTER 1

A.1 Self-Reaction Scheme

Below is the generally accepted mechanism (R. Lee et al., 2016) for the formation of the peroxide accretion product and other self-reaction products.

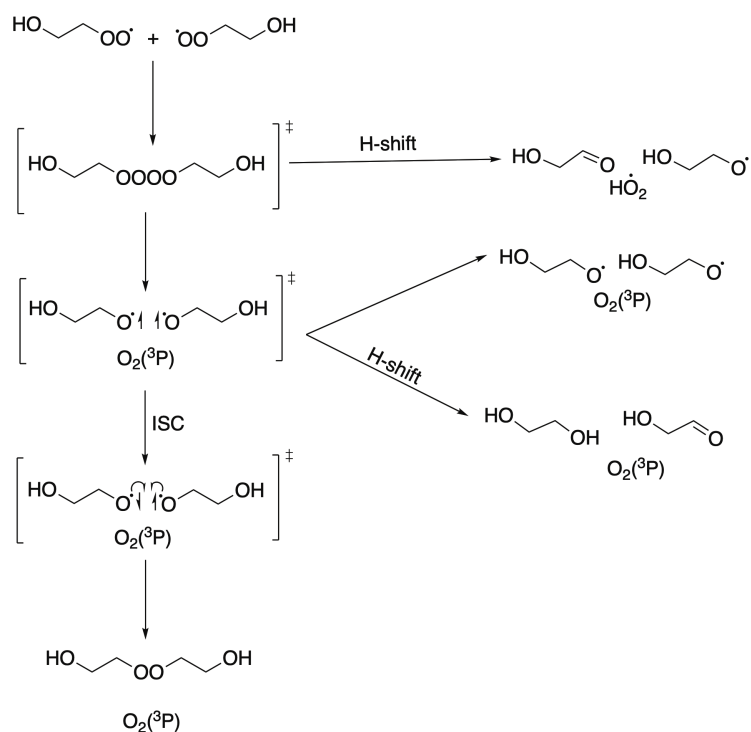


Figure A.1: Peroxy radical self-reaction mechanism, based on the currently proposed mechanism (R. Lee et al., 2016) for these reactions.

A.2 Experimental Conditions

Experiment No.	Exp. Date	[Ethene] ₀	[H ₂ O ₂] ₀	[Methanol] ₀	[2,3-butanediol] ₀
1	1/19/2022	3057	1416	579	0
2	1/21/2022	2923	2057	40000	0
3	1/24/2022	3033	270	1.8	0
4	1/25/2022	3126	686	0	0
5	1/26/2022	3735	655	0	0
6	1/27/2022	3771	1646	1450	0
7	2/8/2022	3045	1377	3500	0
8	2/16/2022	3603	1920	110650	0
9	2/22/2022	3102	1963	4810	0
10	2/28/2022	3077	1944	8961	0
11	3/1/2022	3000	1520	13780	0
12	3/14/2022	3075	1645	78108	0
13	3/16/2022	3073	1919	120200	0
14	3/21/2022	2769	497	0	0
15	3/22/2022	3173	1974	97300	0
16	3/29/2022	3076	2222	88239	0
17	3/29/2022	3074	1322	104.3	0
18	5/17/2022	1827	753	0	6.0
19	6/1/2022	428	966	0	537
20	6/2/2022	479	486	0	631

Table A.1: Experimental conditions for ethene oxidation experiments. All concentrations are in ppbv. All experiments have lights on time of 2 minutes.

A.3 Additional Experimental Results

Photolysis Experiments and Post-Photolysis Dark Decay Rate Frequency. The measured mean photolysis frequency of H₂O₂ in our chamber over a 120 s period of lamp illumination was determined by measuring the OH production via the decay of 2,3 butanediol. We measured the photolysis frequency of glycolaldehyde

by injecting gas-phase glycolaldehyde into the atmospheric chamber along with sufficient methanol to remove any OH produced. The gas-phase glycolaldehyde monomer was prepared by heating solid glycolaldehyde dimer (Sigma Aldrich) in a water bath maintained at 85°C. Upon heating, the glycolaldehyde dimer decomposed to the monomer and was moved and collected in a 200-L Teflon bag using a stream of N₂ gas. A 500-mL glass bulb was filled from the 200-L bag and transferred to the 600-L Teflon chamber bag. We measured the decay rate of the glycolaldehyde irradiated with 8 254 nm UV lamps for approximately 15 minutes (Figure A.2).

ROOH and ROOR mean photolysis frequencies are an average of two 300 s photolysis experiments, performed as described in the main body of the paper. After the lights were turned off, dark decay of both the ROOR and ROOH were observed, in addition to a small rapid increase in the concentration after lights were turned off due to mixing in the bag. The post-photolysis loss was quantified by fitting the decay in each compound after the lights were turned off. These rates were found to be $5.5(\pm 0.8) \times 10^{-5} \text{ s}^{-1}$ for the ROOR and $3.4(\pm 0.7) \times 10^{-5} \text{ s}^{-1}$ for the ROOH. To account for these effects in the calculation of the photolysis frequencies, we corrected the signals of these compounds throughout the experiment with the measured wall loss. The difference between the final and the initial concentration of each compound was then used to calculate the photolysis frequencies. The ROOR and ROOH photolysis data are given in Table A.3. Note that these photolysis frequencies are uncertain, and should be considered to be an upper limit to the true photolysis frequencies of these compounds, since there may be additional losses during these photolysis experiments.

The mean photolysis frequencies listed in the main body of the paper for 120 s experiments are calculated using measurements of the time dependence of the cosine-corrected irradiance measurements (Ocean Optics spectrometer integrated between 224 and 284 nm). The light emission increases over time as the bulbs warm up. Compared to the first 120s, the mean irradiance is 20% and 34% higher for 300 and 900 s experiments, respectively. Table A.2 gives the measured photolysis frequencies and the time over which they were measured, along with the comparison between the mean irradiance over the measured time and the experiment time of 120s.

Assumed Reaction	Mean Photolysis frequency (s^{-1})	Photolysis Time (s)	$\frac{I_t}{I_{120}}$
$\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}$	3.0×10^{-4}	120	1.0
$\text{ROOH} \rightarrow \text{RO} + \text{OH}$	$< 6.3 \times 10^{-4}$	300	1.2
$\text{ROOR} \rightarrow \text{RO} + \text{RO}$	$< 7.3 \times 10^{-4}$	300	1.2
$\text{HOCH}_2\text{CHO} \rightarrow \text{HO}\dot{\text{C}}\text{H}_2 + \text{HCO}$	2.3×10^{-4}	900	1.35

Table A.2: Photolysis reactions. $\text{R} = \text{HOCH}_2\text{CH}_2$. Photolysis time gives the time over which the photolysis frequency was measured. I_t is the mean irradiance of the lights over t seconds, where t is the photolysis time, and I_{120} is the mean irradiance of the lights over 120s.

	Initial [ROOH]	Final [ROOH]	Initial [ROOR]	Final [ROOR]
Experiment 1	5.1	4.2	2.6	1.9
Experiment 2	10.4	8.2	6.3	4.8

Table A.3: ROOR and ROOH photolysis results. All concentrations are reported in ppbv.

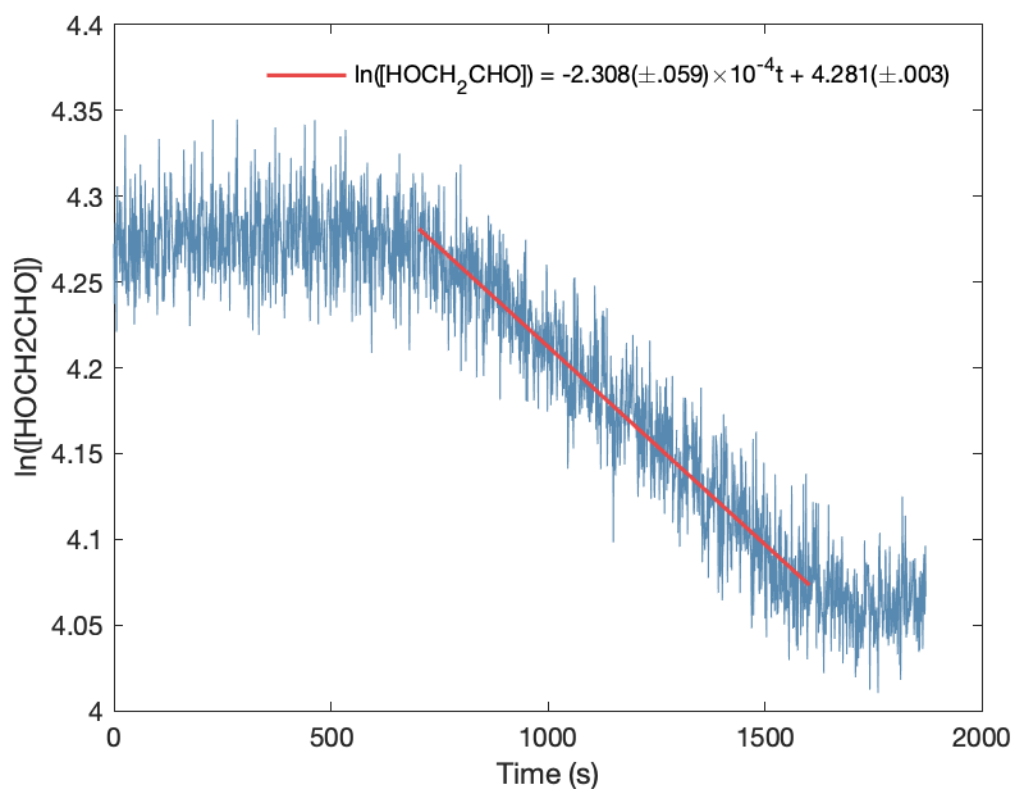


Figure A.2: Decay of glycolaldehyde during photolysis experiment.

Experiments with Steel and Quartz Tubing. The hydroxyhydroperoxide and the accretion product are lost rapidly on quartz and stainless steel. We performed two ethene oxidation experiments in the high RO_2 limit and replaced the Teflon tubing between the bag and the CIMS instrument with approximately 60 cm of 1/4 inch O.D. quartz or steel tubing with a residence time of < 3 s. The results of these experiments are shown in Figure A.3. There is a large loss of the signal at m/z 207 and m/z 163 after the insertion of these tubing materials.

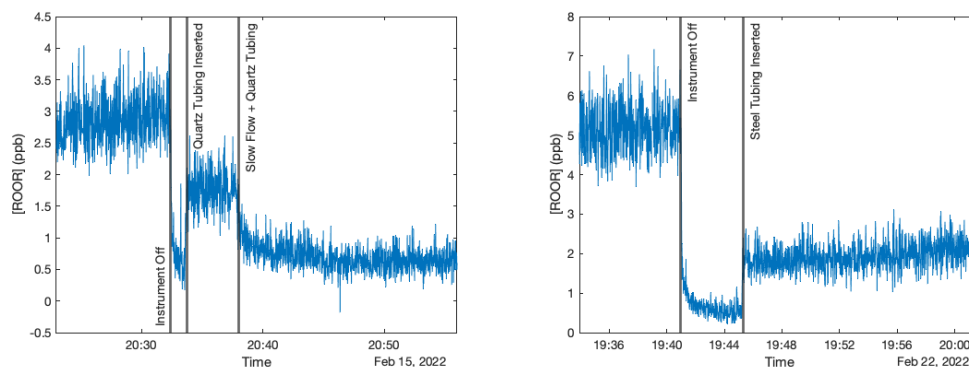
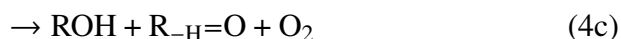
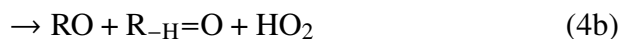
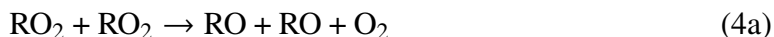
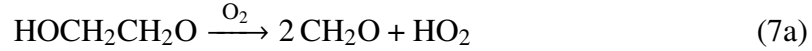


Figure A.3: ROOR concentration before and after insertion of quartz and steel tubing. When quartz tubing was initially inserted, the flow through tubing was approximately 1 L/min, resulting in a residence time of approximately 0.3 s. During the period of slow flow during quartz experiment and in the steel experiment, the flow through the tubing was approximately 200 mL/min, resulting in a residence time of approximately 1.4 s.

Glycolaldehyde Production. More glycolaldehyde than ethylene glycol is produced in the peroxy radical self-reaction, and this excess increases with $[O_2]$. We performed a few experiments in the ‘high RO_2 ’ limit in which we varied the mixing ratio of O_2 and quantified the yields of glycolaldehyde and ethylene glycol. At approximately 1% O_2 , we find the ratio of glycolaldehyde to ethylene glycol formation to be 1.3 ± 0.3 , including uncertainties in sensitivities. To compare the results of our experiments probing the oxygen sensitivity of glycolaldehyde formation to those of Orlando et al. (Orlando, Tyndall, et al., 1998), we compare the derived value of $\frac{k_{7b}[O_2]}{k_{7b}[O_2] + k_{7a}}$ from our experiments (performed at 294K and approximately 740-750 Torr) to that from Orlando et al. at 298K and 700 Torr. To calculate this fraction, we compare the production of ethylene glycol and glycolaldehyde. Recall that the following are the primary reactions that produce glycolaldehyde and ethylene glycol in our system:





Therefore, the production rates of glycolaldehyde and ethylene glycol can be expressed as follows, where GA is glycolaldehyde and EG is ethylene glycol:

$$P_{GA} = k_{7b}[\text{RO}][\text{O}_2] + k_4[\text{RO}_2]^2(\alpha_{4c} + \alpha_{4b})$$

$$P_{EG} = k_4\alpha_{4c}[\text{RO}_2]^2$$

Solving for the steady state concentration of alkoxy radicals ($[\text{RO}]$), where γ is the fraction of thermalized alkoxy radicals in this system (we assume that the fraction of alkoxy radicals that are not stabilized do not form GA):

$$[\text{RO}] = \gamma \frac{k_4\alpha_{4b}[\text{RO}_2]^2 + 2k_4\alpha_{4a}[\text{RO}_2]^2}{k_{7b}[\text{O}_2] + k_{7a}}$$

Substituting this into the equation for the production of glycolaldehyde yields:

$$P_{GA} = k_{7b}\gamma[\text{O}_2] \left(\frac{k_4\alpha_{4b}[\text{RO}_2]^2 + 2k_4\alpha_{4a}[\text{RO}_2]^2}{k_{7b}[\text{O}_2] + k_{7a}} \right) + k_4[\text{RO}_2]^2(\alpha_{4c} + \alpha_{4b})$$

Finally, taking the ratio of P_{GA} to P_{EG} we obtain:

$$\frac{P_{GA}}{P_{EG}} = \gamma \left(\frac{\alpha_{4b} + 2\alpha_{4a}}{\alpha_{4c}} \right) \left(\frac{k_{7b}[\text{O}_2]}{k_{7b}[\text{O}_2] + k_{7a}} \right) + \frac{\alpha_{4c} + \alpha_{4b}}{\alpha_{4c}}$$

Therefore, we can derive $\frac{k_{7b}[\text{O}_2]}{k_{7b}[\text{O}_2] + k_{7a}}$ from the ratio of [GA] to [EG] in our experiments. We determine the y-intercept of this equation by extrapolating our low $[\text{O}_2]$ experiments to $[\text{O}_2] = 0$, and obtain a value of $\frac{\alpha_{4c} + \alpha_{4b}}{\alpha_{4c}} = 1.3 \pm 0.3$. The value of $\frac{\alpha_{4b} + 2\alpha_{4a}}{\alpha_{4c}}$ is determined from the full fit of our box model to our data. The results of this fit (and therefore the resulting values of α_{4b} , α_{4a} , and α_{4c}) are not particularly sensitive to the value of $\frac{k_{7b}[\text{O}_2]}{k_{7b}[\text{O}_2] + k_{7a}}$. We obtain a value of $\frac{\alpha_{4b} + 2\alpha_{4a}}{\alpha_{4c}} = 1.4$. The only remaining unknown is γ . We can estimate γ by comparing our data to that of Orlando et al. (Orlando, Tyndall, et al., 1998), and assuming that $\frac{k_{7b}[\text{O}_2]}{k_{7b}[\text{O}_2] + k_{7a}}$ is equal in both experiments, which yields $\gamma = 0.68$, slightly smaller than $\gamma = 0.74$ determined by Orlando et al. While this may encompass true differences in $\frac{k_{7b}[\text{O}_2]}{k_{7b}[\text{O}_2] + k_{7a}}$, the difference is well within the uncertainty in our estimate of the sensitivities of EG

and GA. Our data is plotted alongside the data of Orlando et al. in Figure A.4, assuming $\gamma = 0.68$. Figure A.4 also shows data from a similar experiments by Barnes et al. (Barnes, Becker, and Ruppert, 1993), who likewise observe an excess of glycolaldehyde at a wide range of $[O_2]$. The low O_2 intercept observed by Barnes et al. varied from 1.4 to 1.6, somewhat higher than, but within the uncertainty of, our results. The intercept of Barnes et al. is pressure dependent and the difference between this intercept and our intercept has been subtracted from the Barnes data in Figure S9. The alkoxy radicals generated in their system were also generated from the RO_2 self-reaction and, at similar pressures, match our results quite closely across the range of $[O_2]$, when the Barnes data is adjusted to match our intercept at 994 hPa. Given the results shown in Figure A.4, in our box model, we use a value of 20% for the branching to reaction with O_2 for the alkoxy reactions in air at 745 Torr and 294K, and assign the low O_2 intercept to a tentative additional reaction pathway of the self-reaction (Reaction 4b). In air, about half of the excess glycolaldehyde is attributed to this additional pathway, albeit with significant uncertainty.

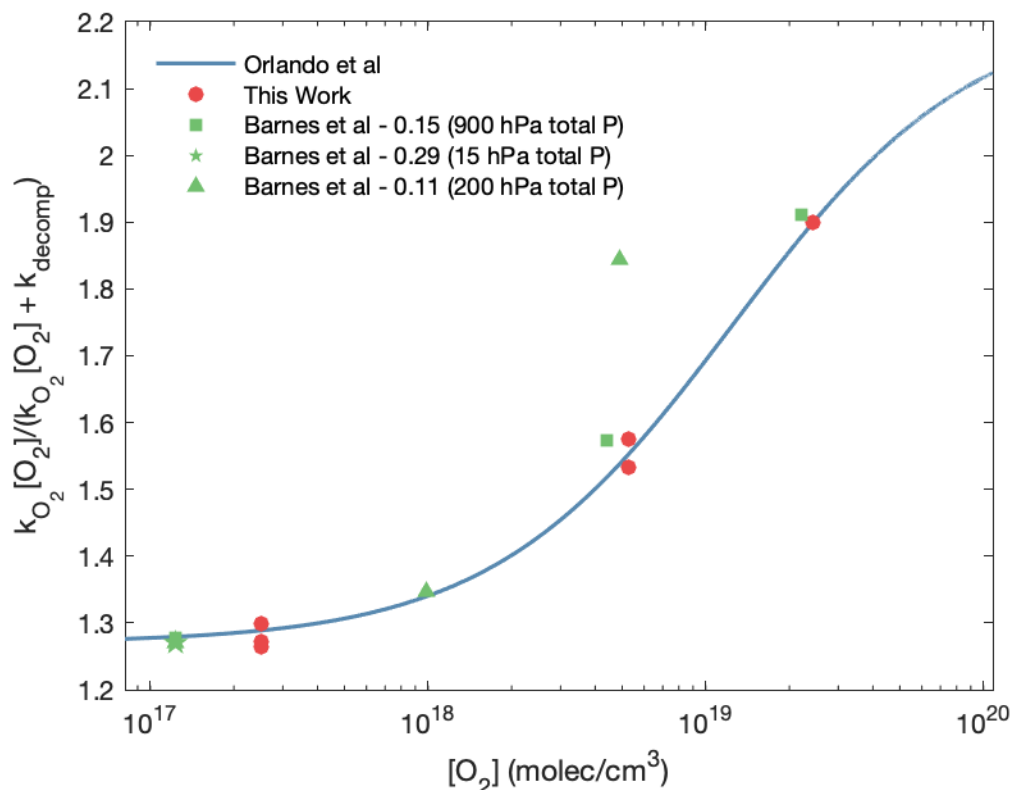


Figure A.4: Fraction of alkoxy radicals that proceed by reaction with O₂, as determined from our data, the data of Barnes et al. (Barnes, Becker, and Ruppert, 1993), and the data of Orlando et al. (Orlando, Tyndall, et al., 1998). The Orlando data is plotted assuming $\gamma = 0.68$ for the yield of thermalized alkoxy radicals at 994 hPa. The data of Barnes et al. are adjusted to match our intercept at low [O₂].

As the primary production of the ROOH relative to the production of glycolaldehyde increases (more HO₂ relative to RO₂), significant glycolaldehyde is produced secondarily via both ROOH photolysis and its reaction with OH. Over the range of HO₂ production for our experiments in air, the box model predicts that the ratio of glycolaldehyde to ethylene glycol will increase by approximately 50% as a result of this secondary production. As illustrated in Figure A.5, the data are consistent with the predictions from the box model. Additionally, the data are consistent with a maximum 0.4% branching to the formation of glycolaldehyde, or a 2% branching to the formation of alkoxy radicals, via this chemistry. This therefore suggests the source of glycolaldehyde formation via the RO₂+HO₂ reaction is quite small. We therefore neglect this source in our analysis. Including this source in our analysis does not change our predicted value of α_{4d} , and changes our predicted value of k_4

by less than 5%.

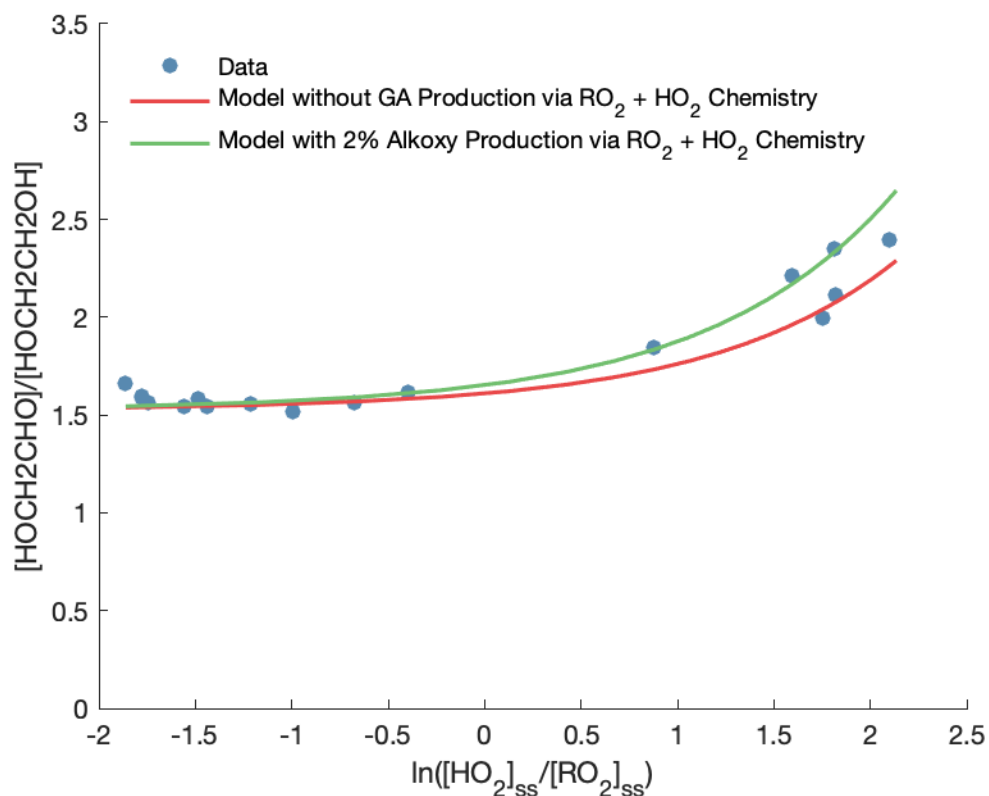


Figure A.5: The ratio between glycolaldehyde and ethylene glycol as a function of the ratio of simulated RO_2 to HO_2 steady state concentration, both as observed and as simulated in the photochemical box model. The red line is the box model run with no glycolaldehyde production via $RO_2 + HO_2$ chemistry. The green line is the box model run with a branching fraction of .02 to the formation of RO and OH via the $RO_2 + HO_2$ reaction or, equivalently, a branching fraction of .004 to the direct formation of glycolaldehyde via the $RO_2 + HO_2$ reaction.

A.4 Reactions, Rate Constants, and Photolysis Frequencies in the Photochemical Box Model

Bimolecular Reaction	Rate Constant ^d ($10^{-12} \frac{cm^3}{molec \cdot s}$)	α	Source
$CH_2=CH_2 + OH \xrightarrow{O_2} HOCH_2CH_2O_2^{\bullet}$	8.1	1	^f
$CH_3OH + OH \xrightarrow{O_2} HO_2 + CH_2O + H_2O$	.90	1	^f
$RO_2 + HO_2 \rightarrow ROOH + O_2$	11	1	Wennberg et al., 2018
$RO_2 + RO_2 \rightarrow ROOR + O_2$	fitted (k_4)	fitted (α_4)	
$\rightarrow 2RO + O_2$		$1 - 3.01\alpha_4$	
$\rightarrow HOCH_2CHO + ROH + O_2$		$1.75\alpha_4$	
$\rightarrow RO + HOCH_2CHO + HO_2$		$0.26\alpha_4$	
$RO \xrightarrow{O_2} HCHO + HO\dot{C}H_2$	^e	0.8	this work
$\xrightarrow{O_2} HOCH_2CHO + HO_2$		0.2	
$HO\dot{C}H_2 + O_2 \rightarrow HCHO + HO_2$	9.1	1	^f
$OH + ROH \xrightarrow{O_2} HOCH_2CHO + HO_2 + H_2O$	14.5	1	Mellouki et al., 2021
$OH + HCHO \xrightarrow{O_2} HO_2 + CO + H_2O$	8.4	1	^f
$OH + HOCH_2CHO \xrightarrow{O_2} HO_2 + O=CHCH=O + H_2O$	11	.2	^f
$\rightarrow HOCH_2C(O)O_2^{\bullet} + H_2O$		.8	^f
$OH + ROOH \rightarrow RO_2 + H_2O$	3.6 ^a	1	
$\xrightarrow{O_2} CH(O)CH_2OOH + HO_2 + H_2O$	7.2 ^b	1	
$\rightarrow HOCH_2CHO + OH + H_2O$	8.2 ^a	1	
$OH + H_2O_2 \rightarrow HO_2 + H_2O$	1.8	1	^f
$OH + HO_2 \rightarrow H_2O + O_2$	110	1	^f
Termolecular Reaction	Rate Constant ^d ($10^{-12} \frac{cm^6}{molec^2 \cdot s}$)	α	Source
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$1.4 + 1.18(1 + (2.5 \times 10^{-6})[H_2O])^c$	1	^f
$HO_2 + HO_2 \cdot CH_3OH \rightarrow H_2O_2 + O_2 + CH_3OH$	$(1.4 \times 10^{-17})[CH_3OH]^c$	1	Christensen et al., 2006

Table A.4: Bimolecular and termolecular reactions and rate constants. R = HOCH₂CH₂. All rate constants are given at 294 K at 993 hPa of air. ^aRate constant used is that of OH + methyl hydroperoxide. ^bRate constant used is 50% that of the total reaction rate constant of OH + ethylene glycol. ^cConcentrations are in units of molecules cm⁻³. ^dTotal reaction rate constant for all reaction channels. ^eThis rate constant is not explicitly included in the box model, and is assumed to be arbitrarily fast. ^fBurkholder et al., 2019

Reaction	Photolysis Frequency (s^{-1})
$\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}$	3.0×10^{-4}
$\text{ROOH} \rightarrow \text{RO} + \text{OH}$	3.0×10^{-4} ^a
$\text{ROOR} \rightarrow \text{RO} + \text{RO}$	3.0×10^{-4} ^a
$\text{HOCH}_2\text{CHO} \rightarrow \text{HO}\dot{\text{C}}\text{H}_2 + \text{HCO}$	1.7×10^{-4}

Table A.5: Photolysis reactions. $\text{R} = \text{HOCH}_2\text{CH}_2$. ^aFor ROOH and ROOR, we use the measured photolysis rate over 120 s for H_2O_2 in the model, as we expect the photolysis rates of these compounds to be similar. We did measure an upper limit to the photolysis rates of these compounds, and these measurements are discussed in Appendix A.3.

Compound	Measured decay rate (s^{-1})
ROOR	5.5×10^{-5}
ROOH	3.4×10^{-5}

Table A.6: Decay in the dark following photolysis. $\text{R} = \text{HOCH}_2\text{CH}_2$

A.5 Levenberg-Marquardt Optimization

Constraint	Value
Step Size Factor for Finite Differences	1×10^{-3}
Function Tolerance	1×10^{-6}
Step Tolerance	1×10^{-6}

Table A.7: Least squares Levenberg-Marquardt optimization parameters.

A.6 GC Conditions

Experiment No.	GC No. ^c	Trap Temperature (°C)	Trap Time (min)	Temperature Ramp	Dilution Factor ^d
6	BG, 1, 2, 3	-45	5	Ramp 1 ^a	4
7	BG	-45	5	Ramp 1	4
	1, 2	-45	10	Ramp 1	4
8	BG	-45	5	Ramp 2 ^b	4
	1	-45	10	Ramp 2	4
9	BG	-45	5	Ramp 2	4
	1, 2	-45	10	Ramp 2	4
10	BG	-45	5	Ramp 2	4
	1	-45	10	Ramp 2	4
11	BG	-45	7	Ramp 2	4
	1	-45	12.8	Ramp 2	4
	2	-45	10	Ramp 2	4
12	BG	-45	5	Ramp 2	4
	1	-45	10	Ramp 2	4
	2	-45	10	Ramp 1	4
13	BG	-45	5	Ramp 1	4
	1	-45	10	Ramp 1	4
	2	-45	10	Ramp 1	5
14	BG	-45	5	Ramp 1	4
	1, 2	-45	10	Ramp 1	4
15	BG	-45	5	Ramp 1	4
	1, 2	-45	10	Ramp 1	4
16	BG	-45	5	Ramp 1	4
	1	-45	10	Ramp 1	4
17	BG	-45	5	Ramp 1	4
	1	-45	5	Ramp 1	6
18	BG	-45	5	Ramp 1	4
	1	-45	5	Ramp 1	6
19	BG	-45	10	Ramp 1	6
	1	-45	3	Ramp 1	8
20	BG	-45	3	Ramp 1	4
	1	-45	5	Ramp 1	4
	2	-40	10	Ramp 1	6

Table A.8: GC conditions in ethene oxidation experiments. ^aTemperature Ramp 1: 15°C/min (-45°C → 10°C), 3 °C/min (10°C → 75°C), 10 °C/min (75°C → 130°C). ^bTemperature Ramp 2: 15°C/min (-45°C → 10°C), 2.5 °C/min (10°C → 45°C), 1.5 °C/min (45°C → 60°C), 10 °C/min (60°C → 130°C). ^cThe GC No. indicates for which GCs of that experiment the listed conditions apply, where BG is the background GC (taken before the lights were turned on), 1 is the first GC after the lights were turned off, etc. ^dThe factor by which the sample of air is diluted with N₂ before being trapped onto the head of the column.

A.7 Peroxide Synthesis and NMR Analysis

NMR Data. Spectral data for hydroxyhydroperoxide **1**: ^1H NMR (400 MHz, CDCl_3) δ 4.16 – 4.13 (AA'XX' m, 2H), 3.92 – 3.90 (AA'XX' m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 78.0, 61.0; IR (thin film, NaCl) 3310, 2944, 1465, 1066, 1031.

Spectral data for ether **2**: ^1H NMR (400 MHz, CDCl_3) δ 4.18-4.16 (AA'XX' m, 2H), 3.80-3.76 (m, 4H), 3.66-3.64 (AA'XX' m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 75.6, 72.7, 68.7, 61.8; IR (thin film, NaCl) 3315, 2916, 1505, 1472, 1443, 1239, 1122, 1069.

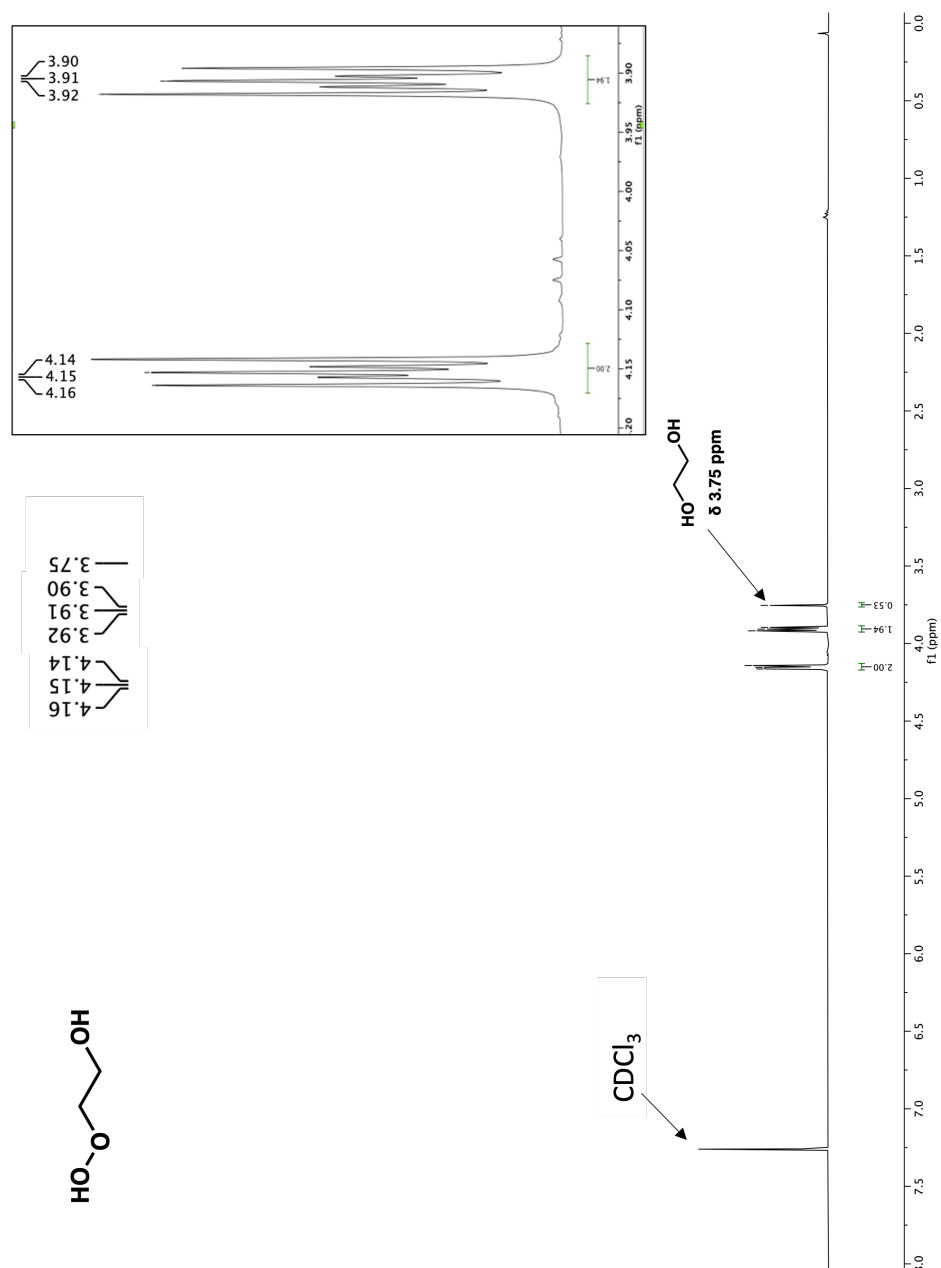


Figure A.6: ^1H NMR (400MHz, CDCl_3) of compound **1**.

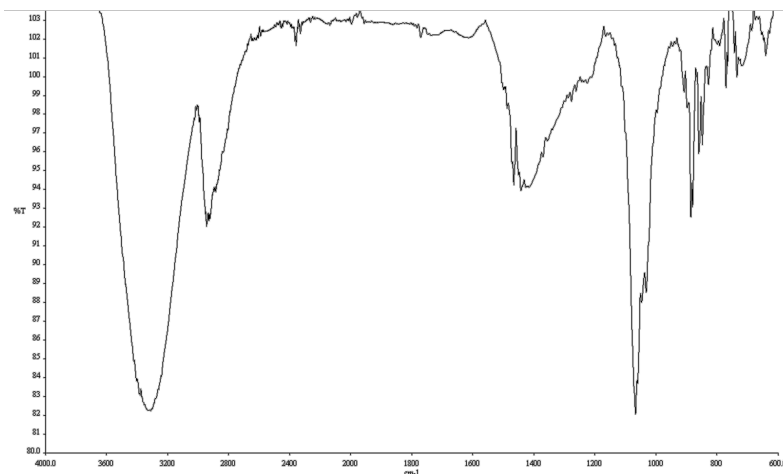


Figure A.7: Infrared spectrum (Thin Film, NaCl) of compound **1**.

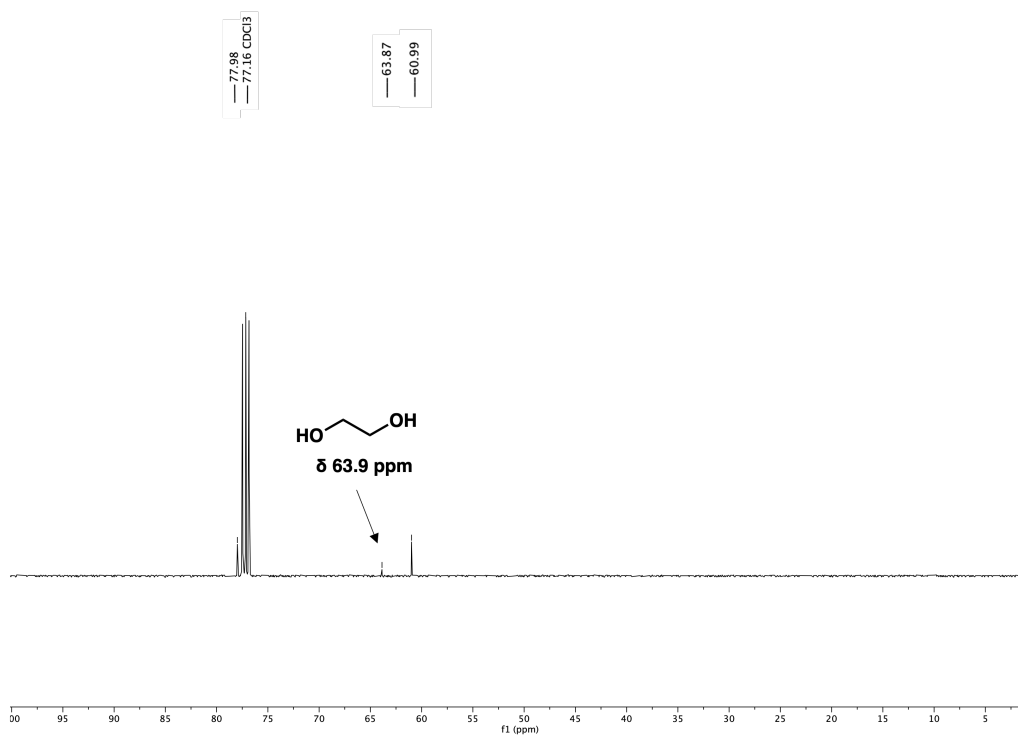
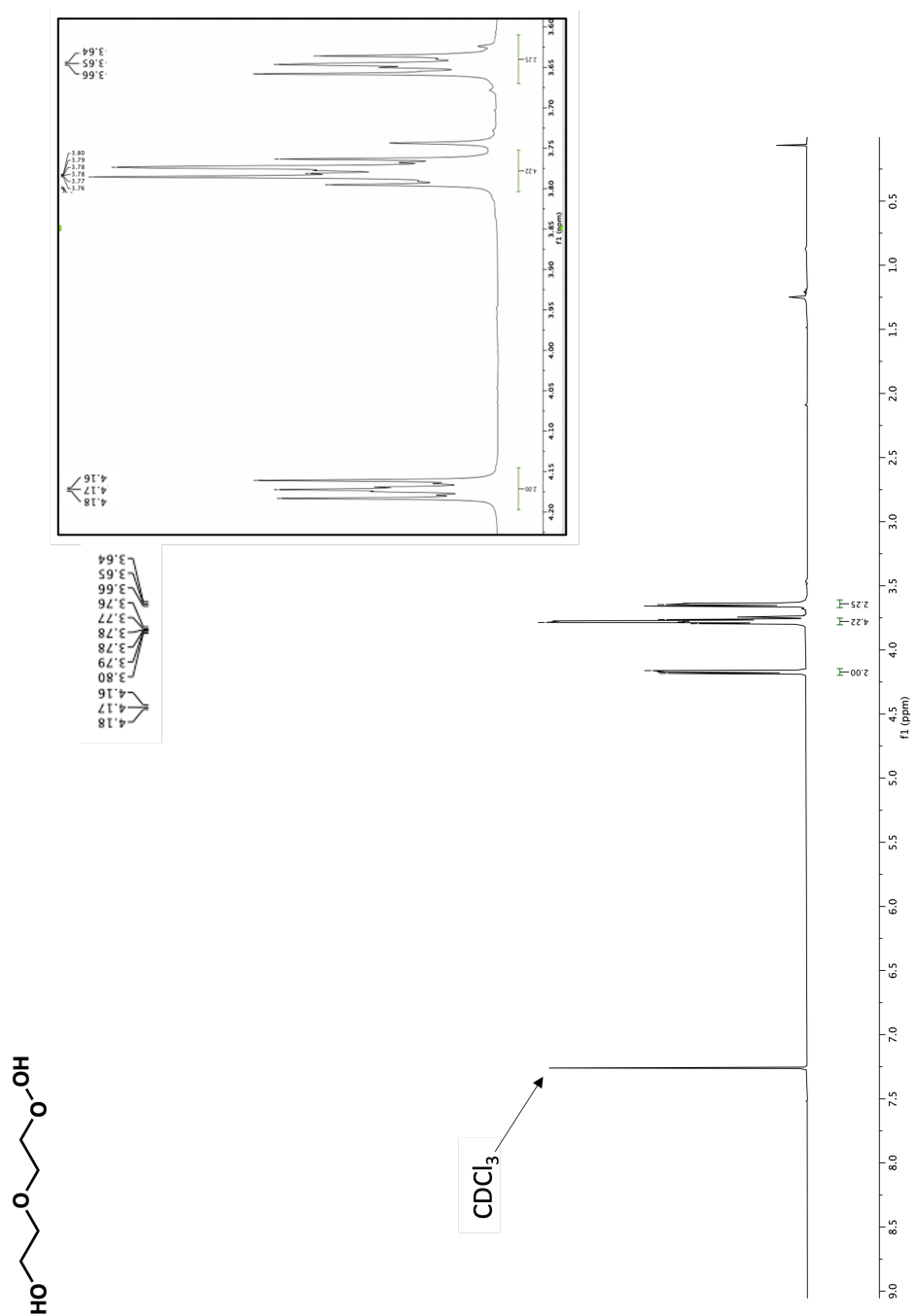


Figure A.8: ¹³C NMR (100 MHz, CDCl₃) of compound **1**.

Figure A.9: ^1H NMR (400 MHz, CDCl_3) of compound **2**.

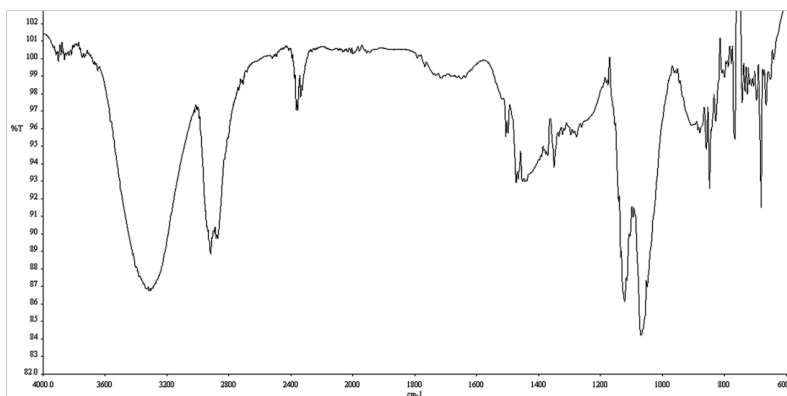


Figure A.10: Infrared spectrum (Thin Film, NaCl) of compound **2**.

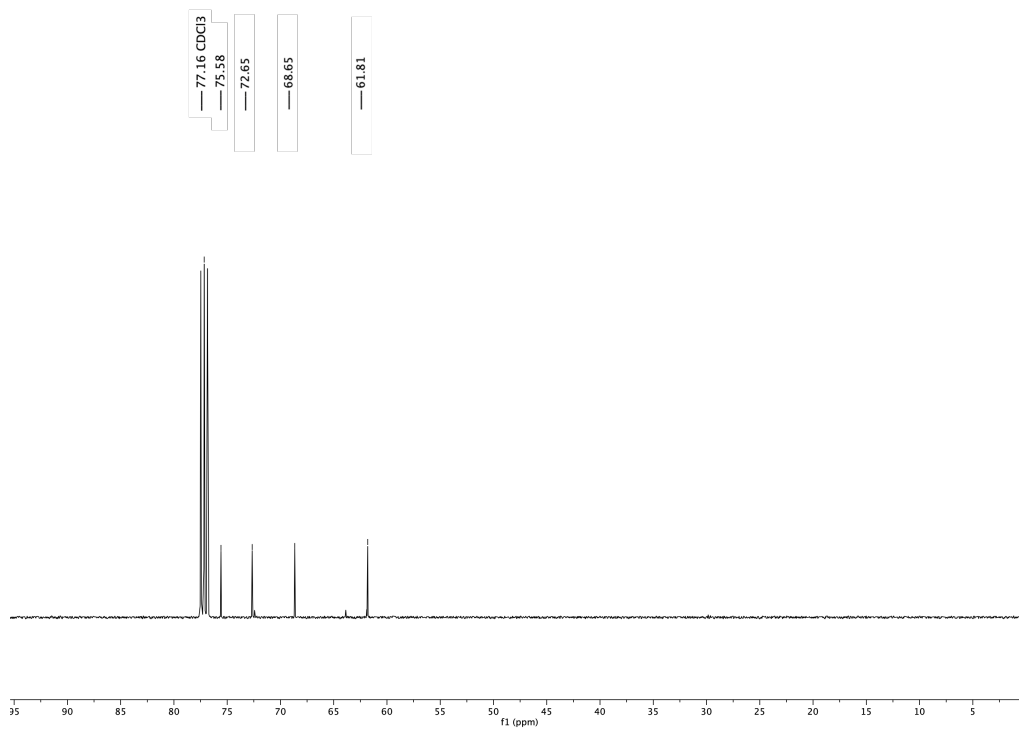


Figure A.11: ^{13}C NMR (100 MHz, CDCl_3) of compound **2**.

A.8 Table of Results

Experiment No.	$\Delta[\text{Ethene}]^a$	F_{external}^b	[ROOR]	[ROH]	[ROOH]	[R _{-H=O}]
1	91	.12	6.2	12.1	28.5	19.3
2	56	1.68	.86	1.8	50.2	3.5
3	19	.02	1.6	3.3	6	5.5
4	48	.05	4.4	7.9	15	12.4
5	46	.04	3.9	7.4	13.7	11.9
6	104	.14	7.7	13.6	38.5	21.1
7	81	.23	5.1	9.3	32.7	14.6
8	31	3.5	.13	.34	25.5	.90
9	107	.31	6.0	10.4	47.3	16.0
10	95	.46	5.2	9.2	56	14.6
11	68	.62	3.5	6.5	43	10.7
12	31	2.94	.29	.55	25.9	1.3
13	26	4.48	.14	.33	22.4	.88
14	31	.04	2.3	4.2	7.2	6.7
15	32	3.55	.19	.43	25.8	1.0
16	37	3.35	.28	.59	35.3	1.3
17	87	.10	7.2	12.2	25.9	18.9
18	49	.10	2.7	6.0	12.8	9.8
19	14	3.60	.18	.25	12.7	.70
20	7	3.48	.09	.20	8.4	.53

Table A.9: Experimental results. All concentrations are in ppbv. ^a $\Delta[\text{Ethene}]$ is determined by the box model. ^b F_{external} is the ratio of HO₂ produced via methanol and H₂O₂ chemistry to the RO₂ produced via the reaction of ethene with OH.

A Note on the Results. An increasing background interference was observed in the ethylene glycol (m/z 147) signal as a function of time after the oxidation period, which most significantly affected the observed ethylene glycol concentrations during experiments with low ethylene glycol production. This background interference was not observed in the GC data. The signal at m/z 149 closely tracked the non-ethylene

glycol background signal at m/z 147. Therefore, we accounted for the non-ethylene glycol background by subtracting the signal at m/z 149 from the m/z 147 signal. Additionally, to increase the signal to noise ratio in the HRTof, the configuration of the instrument was changed in September 2022 to increase the amount of air entering the mass filter ion optics. This resulted in a small change of the observed ratio of glycolaldehyde to ethylene glycol in this study for identical experiments (+10%). As the most careful effort to characterize the CIMS sensitivities to EG and GA occurred after the gas load was increased, we placed the data for all the experiments on a common footing by multiplying the GA concentrations by 1.10 for the data obtained prior to September 2022. We confirmed this correction by replicating an ethylene glycol oxidation experiment and comparing the resulting observed m/z 145 signals before and after the configuration change. Illustrating how sensitive our estimate of α_{4b} is to small changes in the relative sensitivity of GA to ethylene glycol, the 10% increase in GA increased α_{4b} by 50%. The stated uncertainty in α_{4b} is increased to account for this additional source of potential error. Our estimate of the total fraction of radical propagating channels remains the same, as well as our estimate of α_{4c} and α_{4d} . α_{4b} is particularly sensitive to this correction, while other branching fractions are not, due to the method of determining this branching fraction - while other branching fractions are determined from ratios of concentrations, α_{4b} is determined by the difference of two ratios, therefore greatly increasing its uncertainty.

A.9 Mass Balance in Oxidation Experiments

Figure A.12 shows the ratio between the carbon measured in the products and the reacted ethene (predicted by our box model) in our ethene oxidation experiments. The carbon of the measured products is determined by noting that two peroxy radicals are consumed for each ROOR formed, and 2 peroxy radicals are reacted for each ethylene glycol formed. The sum of these should then account for approximately 66% of the carbon produced in the self-reaction. Additionally, one peroxy radical is consumed for each ROOH formed. Figure A.12 demonstrates that our measured products match the reacted ethene quite closely across the range of $F_{external}$.

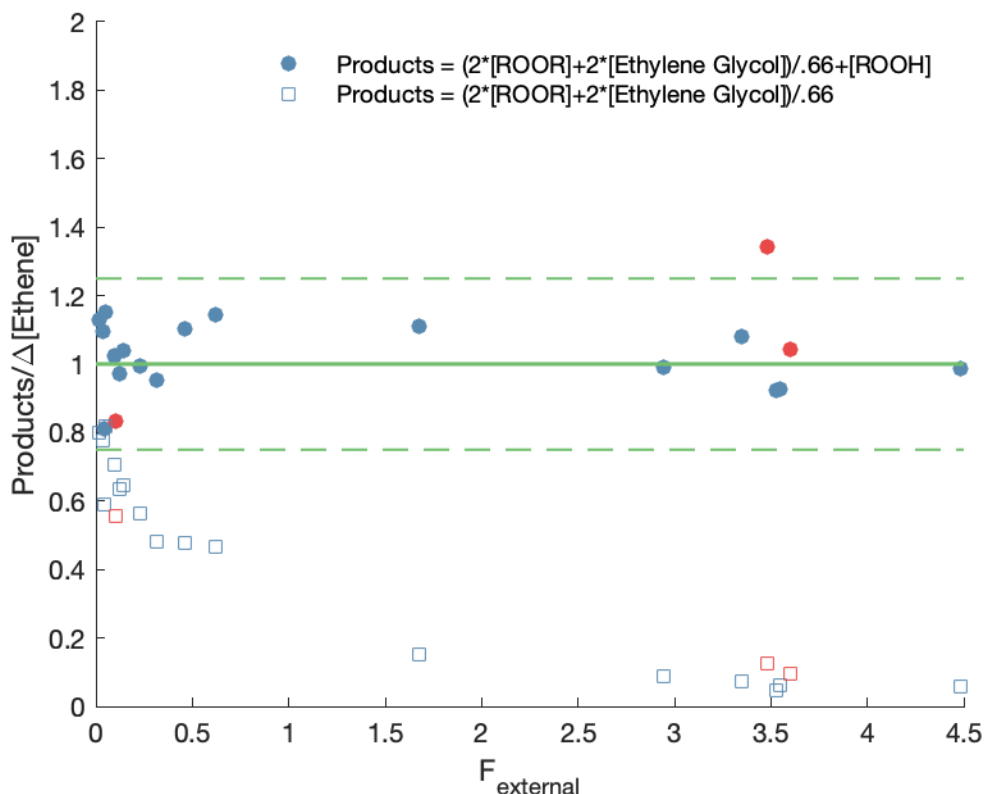


Figure A.12: The ratio between ethene-derived products and $\Delta[\text{Ethene}]$ as a function of F_{external} , where F_{external} is the ratio of HO_2 produced via methanol and H_2O_2 chemistry to the RO_2 produced via the reaction of ethene with OH . Points in blue are experiments performed without butanediol, and points in red are experiments performed with butanediol. Square points include only the carbon from the RO_2 self-reaction in the numerator, while the circle points include the products of the $\text{RO}_2 + \text{HO}_2$ reaction. The solid green line is the line indicating a 1:1 relationship between the measured products and reacted ethene, and the two dashed lines enclose the points within $\pm 25\%$ of mass balance.

A.10 Calculated Polarizabilities and Dipole Moments

The dipole moment and polarizability are calculated at the B3LYP/cc-pVTZ level. The dipole moment is reported below as the weighted averages of the low energy conformers, and the polarizabilities are those of the lowest-energy conformer (Garden et al., 2009). Using these dipole moment and polarizability estimates, ion-molecule collision rate coefficients ($k_{\text{cap}}(T)$) are calculated using the parameterization of Su et al. (Su and Chesnavich, 1982) (Equations A.3 - A.6), where q is the charge of the electron, α is the polarizability of the molecule, μ_D is the dipole moment, μ is the reduced mass of the molecule and the ion, k_B is the Boltzmann constant, and T is

the temperature.

$$k_L = 2\pi q \sqrt{\frac{\alpha}{\mu}} \quad (\text{A.3})$$

$$x = \frac{\mu_D}{\sqrt{2\alpha k_B T}} \quad (\text{A.4})$$

$$K_{cap} = \begin{cases} 0.4767x + 0.6200 & x \geq 2 \\ \frac{(x+0.5090)^2}{10.526} + 0.9754 & x \leq 2 \end{cases} \quad (\text{A.5})$$

$$k_{cap}(T) = K_{cap} \times k_L \quad (\text{A.6})$$

Compound	α ($\text{\AA}^3$)	μ_D (D)	Collision Rate Coefficient ($10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)
Ethylene glycol	5.11	2.08	1.91
H ₂ O ₂	1.78	1.77	1.78
2,3-butanediol	8.6	2.2	1.94
2-hydroxy-3-butanone	8.10	3.09	2.46
Glycolaldehyde	4.64	2.33	2.06
HOCH ₂ CH ₂ OOCH ₂ CH ₂ OH	10.16	2.45	2.01
HOCH ₂ CH ₂ OOH	5.91	2.44	2.05
Diethylene Glycol	9.34	2.17	1.88

Table A.10: Calculated polarizabilities, dipole moments, and CF₃O[−]-molecule collision rate coefficients for compounds of interest. T = 298K

A.11 Calculation of Uncertainties

Sensitivities

For the measured sensitivities, the uncertainty is calculated as a standard deviation of replicate measurements. In the case of 2,3-butanediol, where only one measurement was taken, the error in the sensitivity is calculated by propagating the error from the measured weight of the compound and the uncertainty in the CIMS signal. Similarly, the error in 2-hydroxy-3-butanone was determined by propagating the error in the CIMS signal and the error in the 2,3-butanediol concentration. The

error of the calculated sensitivities was determined by propagating the error of the ethylene glycol sensitivity, from which they were calculated.

Photolysis Rates

Uncertainties in the photolysis rates of ROOH and ROOR are derived from the standard deviation of the two measurements. Uncertainties in the photolysis frequencies of H_2O_2 and glycolaldehyde are determined by the uncertainty in the fitted slopes used to determine these photolysis frequencies.

Self-Reaction Parameters

The error in the self-reaction parameters is calculated by propagating the errors from the various error sources, as listed in the main body of the paper. The error of each of these constraints was determined as follows.

1. **Q**: Determined by propagating the errors in the post-oxidation CIMS signals and the errors in the sensitivities of each of the compounds. The error in the CIMS signals was determined to be the standard deviation of the signal during the equilibration period.
2. **F_{external}** : Determined by propagating the errors in the ethene, methanol, and H_2O_2 concentrations, which each have errors of 10%, and the rate constants of each of their reactions with OH, which each have errors of 15%.
3. **Fit**: Determined using a bootstrapping method.
4. **Ratios of Sensitivities**: Determined by propagating the errors of the individual sensitivities, which are calculated as described above.

Appendix B

SUPPLEMENTARY INFORMATION FOR CHAPTER 2

B.1 GC Conditions

Experiment No.	GC No. ^a	Trap Temperature (°C)	Trap Time (min)	Dilution Factor ^b
1	BG	-30	2	4
	1	-20	2	2
2	BG	-30	2	4
	1	-30	2	2
	2	-10	10	2
	3	-40	2	5
3	BG, 1, 2	-30	2	2
	3	-35	2	2
4	BG	-30	2	2
	1	-30	2.2	2
	2	-30	2	4
	3	-30	2	5
5	BG, 1, 2	-30	2	4
	3	-10	10	4
6	BG	-30	1	4
	1	-30	2	2
	2	-30	2	4
	3	-10	10	2

Table B.1: GC conditions for methyl propene oxidation experiments. For all experiments given here, the following temperature ramp was used: 15°C/min (Trap T → 10°C), 4 °C/min (10°C → 90°C), 10 °C/min (90°C → 130°C). ^aThe GC No. indicates for which GCs of that experiment the listed conditions apply, where BG is the background GC (taken before the lights were turned on), 1 is the first GC after the lights were turned off, etc. ^bThe factor by which the sample of air is diluted with N₂ before being trapped onto the head of the column.

Experiment No.	GC No. ^c	Trap Temperature (°C)	Trap Time (min)	Temperature Ramp	Dilution Factor ^d
1	BG, 1	-30	2	Ramp 1 ^a	4
	2	-30	2	Ramp 1	5
	3	-30	2	Ramp 2 ^b	6
2	BG	-30	2	Ramp 1	4
	1	-30	2	Ramp 1	3
	2	-30	3	Ramp 1	4
	3	-10	10	Ramp 2	3
3	BG	-30	1	Ramp 1	4
	1	-30	2	Ramp 1	2
	2	-30	2	Ramp 1	4
4	BG, 1	-30	2	Ramp 1	2
	2	-30	2	Ramp 2	2
	3	-10	10	Ramp 2	2
5	BG	-30	2	Ramp 1	2
	1	-30	2	Ramp 1	4

Table B.2: GC conditions for cis-2-butene oxidation experiments. ^aRamp 1: 15°C/min (Trap T → 10°C), 4 °C/min (10°C → 90°C), 10 °C/min (90°C → 130°C). ^bRamp 2: 15°C/min (Trap T → 15°C), 2.5°C/min (15°C → 90°C), 10 °C/min (90°C → 130°C). ^cThe GC No. indicates for which GCs of that experiment the listed conditions apply, where BG is the background GC (taken before the lights were turned on), 1 is the first GC after the lights were turned off, etc. ^dThe factor by which the sample of air is diluted with N₂ before being trapped onto the head of the column.

Experiment No.	GC No. ^c	Trap Temperature (°C)	Trap Time (min)	Temperature Ramp	Dilution Factor ^d
1	BG	-45	5	Ramp 1 ^a	4
	1	-45	10	Ramp 1	4
	2, 3	-45	10	Ramp 2 ^b	4
2	BG	-45	5	Ramp 2	4
	1, 2	-45	10	Ramp 2	4
3	BG	-45	5	Ramp 2	4
	1	-45	10	Ramp 2	4
4	BG	-45	5	Ramp 2	4
	1, 2	-45	10	Ramp 2	4
5	BG	-45	5	Ramp 2	4
	1	-45	10	Ramp 2	4

Table B.3: GC conditions for propene oxidation experiments. ^aRamp 1: 15°C/min (Trap T → 10°C), 3 °C/min (10°C → 75°C), 10 °C/min (75°C → 130°C). ^bRamp 2: 15°C/min (Trap T → 10°C), 2.5°C/min (10°C → 45°C), 1.5°C/min (45°C → 60°C), 10 °C/min (60°C → 130°C). ^cThe GC No. indicates for which GCs of that experiment the listed conditions apply, where BG is the background GC (taken before the lights were turned on), 1 is the first GC after the lights were turned off, etc. ^dThe factor by which the sample of air is diluted with N₂ before being trapped onto the head of the column.

B.2 Sensitivities and Ion-Molecule Collision Rates

Compound	Calc. CF_3O^- -molecule collision rate ^a
Ethylene glycol	1
H_2O_2^c	0.94
2,3-butanediol	1.02
2-hydroxy-3-butanone	1.29
Glycolaldehyde	1.08
$\text{HOCH}_2\text{CH}_2\text{OOCH}_2\text{CH}_2\text{OH}$	1.05
$\text{HOCH}_2\text{CH}_2\text{OOH}$	1.08
Propylene Glycol	1.08
Hydroxy Acetone	1.31
2-hydroxy-propanal	1.10
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OOH}$	1.06
$\text{CH}_3\text{CH}(\text{OOH})\text{CH}_2\text{OH}$	1.12
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OOCH}_2\text{CH}(\text{OH})\text{CH}_3$	1.05
$\text{CH}_3(\text{CH}_2\text{OH})\text{CHOOCH}_2\text{CH}(\text{OH})\text{CH}_3$	1.03
$\text{CH}_3(\text{CH}_2\text{OH})\text{CHOOCH}(\text{CH}_2\text{OH})\text{CH}_3$	1.03

Table B.4: Calculated relative ion-molecule collision rate coefficients. ^aRelative to ethylene glycol. ^bThe ratio of sensitivity to ethylene glycol is lower than the ratio of the ion-molecule collision rate coefficients due to incomplete stabilization of collisions (Crounse, McKinney, et al., 2006).

B.3 GC Transmission Efficiencies

Compound	Elution T	Trap T (°C)	Min Avg Transmission	Max Avg Transmission
MP-ROOH	59	-10	51(± 2)%	53(± 2)%
		-20	76%	78%
		-30	83(± 6)%	83(± 7)%
E-ROOH	52	-10	20(± 1)%	22(± 1)%
		-20	53%	56%
		-30	50(± 5)%	58(± 5)%
B-ROOH	61	-10	30(± 25)%	33(± 28)%
		-20	9%	10%
		-30	44(± 33)%	50(± 38)%
MP-ROH	33.4	-30	64.5(± 0.7)%	66.5(± 0.7)%
B-ROH	35	-10	1%	1%
		-20	5%	7%
		-30	11(± 6)%	13(± 6)%
MP-ROOR	79.5	-10	82(± 25)%	94(± 20)%
		-30	86(± 17)%	121(± 41)%
E-ROOR	75	-10	44(± 2)%	53(± 5)%
		-20	40%	60%
		-30	27(± 7)%	41(± 8)%
B-ROOR	84	-10	35(± 27)%	
		-20	7%	
		-30	38(± 27)%	
MP+E ROOR	78	-10	66(± 1)%	68%
		-20	80	
		-30	65(± 10)%	65.5(± 0.7)%
B+E ROOR	80	-10	59%	
		-30	59(± 8)%	

Table B.5: Calculated transmission efficiencies for various compounds in the 2m GC-CIMS. The transmission is calculated by finding the ratio between the signal measured during direct sampling and the integrated GC signal, accounting for the different dilutions and flows. Minimum average transmissions are calculated by neglecting tailing in the fit, while maximum transmissions are calculated by fitting to the tailing. For those compounds with minimal tailing, only a minimum average transmission is given. Uncertainties are the standard deviations of multiple measurements.

B.4 GC Best-Fit Parameters

The following tables give the bootstrap best fit parameters for fits used in the main analysis. Fits are performed using a modified version of an open-source Matlab peak fitting function (O'Haver, 2017) and are fit to an exponentially decaying Gaussian peak shape with varying widths and time constants.

Date	GC	m/z	Time Constant	Width	Area	Error	R ²
9/25/2023	1	191	[7.9 6.5]	[11.39 13.55]	[14.48 66.34]	1.57%	0.99
		235	[13.3 22.5]	[15.60 19.61]	[0.087 0.024]	4.92%	0.92
9/28/2023	1	191	[7.5 7.2]	[13.3 13.8]	[17.13 83.6]	1.44%	0.99
		235	[12.3 22.5]	[16.8 28.7]	[0.14 0.058]	5.10%	0.93
	2	191	[6.7 8.1]	[15.6 11.7]	[46.6 266.2]	1.35%	1.00
		235	[11.2 16.2]	[15.0 28.1]	[0.64 0.15]	2.04%	0.99
	3	263	[10.4 9.0 13.5]	[15.2 16.3 6.3]	[0.032 0.050 0.0042]	6.81%	0.90
		191	[7.2 9.8]	[12.1 13.3]	[5.53 30.74]	1.76%	0.99
10/05/2023	1	235	[22.2 22.2]	[15.9 29.1]	[0.044 0.016]	9.40%	0.69
		191	[14.9 7.5]	[7.7 13.4]	[2.10 55.32]	1.44%	1.00
	2	263	[7.0 9.5 8.6]	[18.2 12.1 22.9]	[0.14 1.52 0.50]	1.54%	1.00
		191	[7.6 10.8]	[13.9 5.6]	[1.72 55.75]	1.54%	1.00
	3	263	[8.6 11.6 6.1]	[7.5 16.3 21.8]	[0.13 1.37 0.37]	1.91%	0.99
		191	[6.7 9.8]	[13.7 10.9]	[1.70 50.35]	1.36%	1.00
10/08/2023	1	263	[9.2 7.4 8.2]	[16.9 23.3 21.6]	[0.13 1.24 0.39]	1.78%	0.99
		191	[7.2 8.1]	[13.5 13.8]	[15.15 74.83]	1.60%	0.99
	2	263	[11.4 12.8 15.0]	[30.0 14.9 24.6]	[0.041 0.067 0.034]	9.21%	0.82
		191	[7.6 7.7]	[13.3 14.0]	[14.96 73.69]	1.50%	0.99
	3	263	[10.8 9.0 5.5]	[16.1 14.5 17.5]	[0.015 0.051 0.020]		
		191	[6.6 6.8]	[13.4 14.6]	[39.55 227.10]	1.39%	0.99
10/23/2023	1	263	[5.7 10.5 13.6]	[20.0 18.0 19.4]	[0.084 0.26 0.15]	4.22%	0.97
		191	[8.6 9.0]	[13.9 11.4]	[12.38 68.27]	1.96%	0.99
	2	235	[16.1 21.6]	[15.4 27.0]	[0.12 0.036]	3.4%	0.98
		191	[8.5 9.0]	[13.9 11.4]	[12.38 68.27]	1.96%	0.99
	3	235	[14.9 21.4]	[17.0 22.8]	[0.077 0.021]	4.50%	0.95
		191	[8.1 7.0]	[14.7 14.6]	[43.21 230.6]	1.41%	1.00
	263	235	[11.7 18.3]	[16.0 26.5]	[0.78 0.19]	1.61%	0.99
		263	[12.1 12.6 12.3]	[15.4 15.7 15.9]	[0.036 0.062 0.0031]	4.53%	0.96

Table B.6: Bootstrap best fit parameters for GCs in methylpropene and ethene oxidation experiments. Only results for those fits that were used in the main analysis are given. Where multiple fits were performed, that with the minimum error is given here.

Date	GC	m/z	Time Constant	Width	Area	Error	R ²
10/09/2023	1	191	12.3	12.0	3.33	2.43%	0.98
		263	16.9	22.3	0.095	2.21%	0.99
		175	[14.8 13.5]	[7.2 9.3]	[0.32 0.43]	5.71%	0.91
	2	191	12.3	12.0	2.52	2.48%	0.98
		263	18.2	22.5	0.066	2.39%	0.99
		175	[6.2 14.9]	[10.5 9.0]	[0.18 0.40]	5.92%	0.91
	3	191	14.9	20.3	1.91	3.02%	0.98
		263	21.8	37.4	0.047	2.76%	0.99
		175	[5.6 14.9]	[15.3 15.1]	[0.10 0.29]	8.80%	0.83
10/11/2023	1	191	9.9	12.6	22.15	2.16%	0.99
		263	15.4	25.0	0.0088	6.58%	0.87
		175	[10.2 29.7]	[12.6 8.6]	[0.018 0.052]	5.81%	0.78
	2	191	9.6	11.8	21.95	2.11%	0.99
		263	14.3	26.9	0.0075	7.62%	0.86
		175	[6.9 29.1]	[16.1 9.1]	[0.020 0.060]	5.40%	0.84
	3	191	10.9	20.4	69.35	1.81%	0.99
		263	22.9	37.4	0.032	4.53%	0.97
		175	[7.7 29.0]	[15.7 15.1]	[0.0014 0.030]	5.68%	0.74
10/26/2023	1	191	10.7	11.9	80.18	2.34%	0.99
		235	22.4	17.2	0.094	5.35%	0.93
		263	10.2	29.7	0.015	12.02%	0.59
	2	191	11.4	10.7	31.62	3.05%	0.97
		235	22.4	16.8	0.0046	6.42%	0.88
		263	10.2	29.7	0.015	12.02%	0.59
11/01/2023	1	191	9.3	12.4	94.12	2.07%	0.99
		235	22.4	17.9	0.14	4.15%	0.96
		263	18.1	22.0	0.024	9.43	0.72
		175	[9.8 27.6]	[16.1 16.3]	[0.11 0.22]	5.52%	0.84
	2	191	9.7	11.0	82.77	2.15%	0.99
		235	22.4	17.7	0.12	4.11%	0.96
		263	11.1	26.4	0.017	10.50%	0.67
		175	[13.8 29.4]	[9.8 16.1]	[0.17 0.11]	6.64%	0.81
		263	10.2	29.7	0.015	12.02%	0.59

Table B.7: Bootstrap best fit parameters for GC peaks in cis-2-butene and ethene oxidation experiments. Only results for those fits that were used in the main analysis are given. Where multiple fits were performed, that with the minimum error is given here.

Date	GC	m/z	Time Constant	Width	Area	Error	R ²
2/9/2022	1	177	[14.1 9.5]	[27.7 33.2]	[10.80 47.69]	2.07%	0.99
		221	[24.3 30.7]	[26.2 37.0]	[5.45 4.04]	5.21%	0.96
		235	[19.6 16.0 36.1]	[36.9 40.5 35.5]	[1.01 2.18 0.73]	5.82%	0.91
	2	177	[14.8 11.9]	[33.3 35.7]	[13.17 56.39]	2.17%	0.99
		221	[35.2 22.5]	[37.5 42.0]	[5.72 4.45]	7.04%	0.94
		235	[31.3 25.4 28.8]	[52.5 50.8 38.2]	[1.33 2.25 0.64]	7.50%	0.89
	3	177	[10.5 9.3]	[32.8 37.3]	[11.29 54.89]	2.34%	0.99
		221	[37.2 27.8]	[37.4 41.6]	[5.05 4.03]	6.87%	0.94
		235	[42.1 43.2 35.9]	[51.2 46.6 18.3]	[1.28 2.20 0.45]	8.51%	0.83
2/10/2022	1	177	[13.1 11.2]	[40.0 35.5]	[18.0 83.7]	2.15%	0.99
		221	[40.5 20.3]	[37.4 40.9]	[5.41 4.05]	5.90%	0.95
		235	[34.8 15.9 31.8]	[54.2 57.9 50.6]	[3.85 7.25 2.91]	4.94%	0.96
	2	177	[9.7 11.8]	[36.0 35.7]	[16.3 84.7]	2.03%	0.99
		221	[38.0 26.6]	[42.6 35.4]	[4.97 3.83]	5.69%	0.95
		235	[40.8 34.3 33.2]	[51.5 48.0 36.2]	[3.79 7.41 1.79]	4.85%	0.95
2/11/2022	1	177	[10.4 7.7]	[34.4 37.5]	[82.88 235.3]	2.24%	0.99
		221	[28.3 25.7]	[44.7 38.4]	[8.80 4.50]	4.79%	0.96
		235	[19.6 21.2 41.6]	[66.4 44.8 41.9]	[1.96 2.23 0.50]	7.00%	0.89
2/14/2022	1	177	[11.4 8.3]	[32.1 37.4]	[47.89 167.5]	2.32%	0.99
		221	[38.2 24.0]	[43.7 34.6]	[5.22 2.74]	6.23%	0.94
		235	[16.2 23.2 40.5]	[57.6 56.3 38.1]	[2.99 5.06 1.13]	6.11%	0.94
	2	177	[13.3 9.6]	[30.6 38.2]	[39.14 138.1]	2.37%	0.99
		221	[33.5 23.1]	[44.4 41.8]	[3.52 2.12]	7.78%	0.91
		235	[19.6 30.3 29.9]	[57.8 49.0 29.1]	[2.31 3.72 0.56]	6.49%	0.92

Table B.8: Bootstrap best fit parameters for propene and ethene oxidation experiments. Only results for those fits that were used in the main analysis are given. Where multiple fits were performed, that with the minimum error is given here.

B.5 ID of Butanediol Stereoisomers

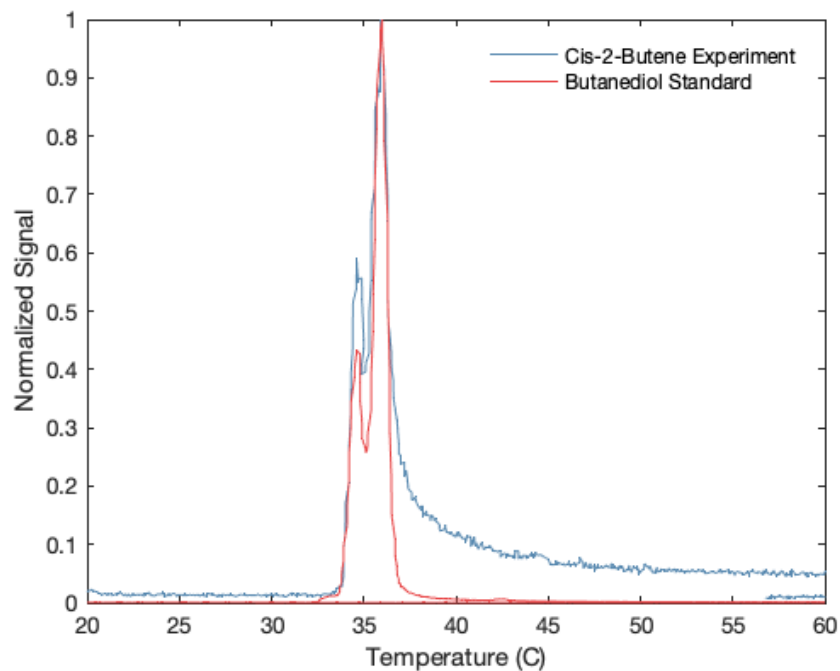


Figure B.1: Comparison of chromatogram of m/z 175 formed in the oxidation of cis-2-butene during experiment performed on 10/9/2023 (blue trace) with chromatogram of 2,3-butanediol standard (red trace). The standard contains a mix of stereoisomers.

We can see in Figure B.1 that both peaks at m/z 175 in the oxidation of cis-2-butene in the presence of OH can be attributed to stereoisomers of 2,3-butanediol. However, the experimental chromatogram shows a significantly long tail that is not present in the chromatogram from the oxidation experiment. Below (Figure B.2) we see that this tailing is due to a distinct compound. Throughout the GC, we can see that a compound with a distinct exact mass grows in while the the signal that can be attributed to 2,3-butanediol decreases.

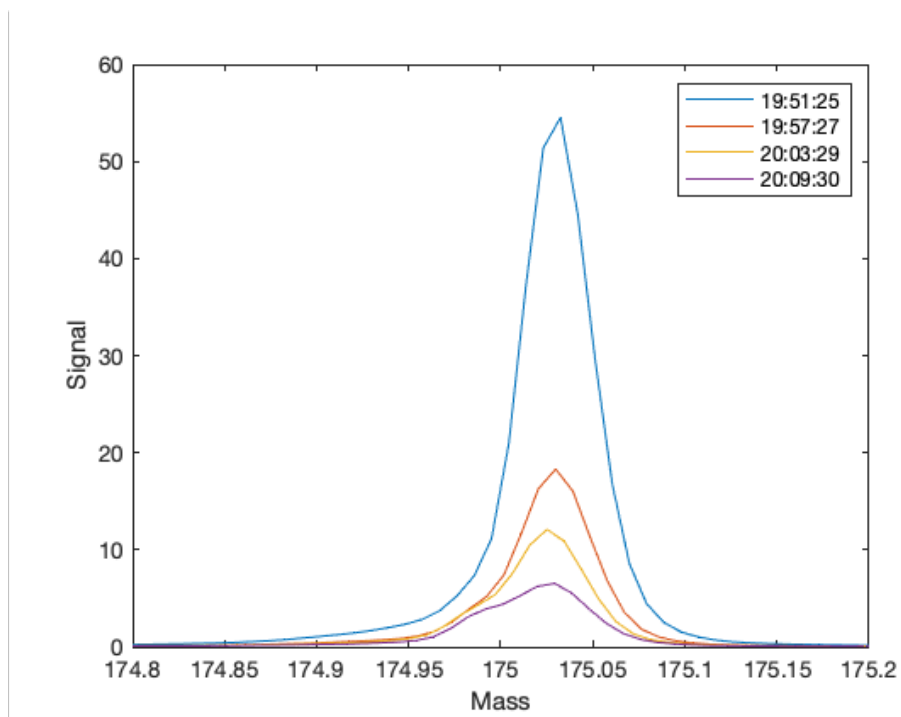


Figure B.2: Plot of high resolution mass spectral data from the oxidation of *cis*-2-butene during experiment on 10/9/2023. The legend shows the time at which the data collection for each trace began. The earliest trace began at approximately the time that *m/z* 175 during the first chromatogram following oxidation.

In order to account for the tail in plots of the butanediol stereoisomers, the tail is fit to a third peak, and the fitted peak accounting for the tail was subtracted from the overall signal.

B.6 Tables of Results

	[ROOR] _{MP}	[ROH] _{MP}	[ROOH] _{MP}	[R _{-H=O}] _{MP}	[ROOR] _E	[ROH] _E	[ROOH] _E	[R _{-H=O}] _E	[ROOR] _{Cross}
1	0.0040	0.37	21	0.26	0.045	0.41	14	1.4	0.029
2	0.0063	0.59	24	0.31	0.095	0.70	20	1.9	0.053
3	0.58	4.3	13	1.5	0	0	0	0	0
4	0.49	3.2	10	1.1	0	0	0	0	0
5	0.036	0.63	42	0.53	0	0	0	0	0
6	0.0064	0.96	23	0.32	0.11	1.2	22	2.7	0.062

Table B.9: Experimental results for experiments with methylpropene and ethene as precursors. Note that in this table MP = methylpropene and E = ethene and "cross" indicates the product formed in the cross reaction of ethene- and methylpropene-derived peroxy radicals. All concentrations are in ppbv.

	[ROOR] _B	[ROH] _B	[ROOH] _B	[R _{-H=O}] _B	[ROOR] _E	[ROH] _E	[ROOH] _E	[R _{-H=O}] _E	[ROOR] _{Cross}
1	0.42	5.3	12.6	4.7	0	0	0	0	0
2	0.014	0.23	36	0.50	0	0	0	0	0
3	0.0053	0.30	19	0.27	0.089	0.89	17.5	1.9	0.036
4	0.0064	0.32	23	0.30	0.10	0.85	19	1.9	0.041
5	0.23	3.2	7.8	3.9	0	0	0	0	0

Table B.10: Experimental results for experiments with cis-2-butene and ethene as precursors. Note that in this table B = cis-2-butene and E = ethene and "cross" indicates the product formed in the cross reaction of ethene- and cis-2-butene-derived peroxy radicals. All concentrations are in ppbv.

	[ROOR] _P	[ROH] _P	[ROOH] _P	[R _{-H=O}] _P	[ROOR] _E	[ROH] _E	[ROOH] _E	[R _{-H=O}] _E	[ROOR] _{Cross}
1	1.1	5.0	15	5.9	1.9	7.0	9.1	9.0	2.8
2	2.8	9.3	20	9.8	0.45	3.7	4.2	4.7	2.2
3	0.95	4.3	60	5.1	2.2	7.3	49	11.3	2.8
4	1.5	4.5	36	4.7	0.38	2.5	8.9	4.4	1.5
5	0.30	1.3	30	1.6	0.65	2.3	25	4.1	0.88

Table B.11: Experimental results for experiments with propene and ethene as precursors. Note that in this table P = propene and E = ethene and "cross" indicates the product formed in the cross reaction of ethene- and propene-derived peroxy radicals. All concentrations are in ppbv.

B.7 Experimental Conditions

Exp. No.	Exp. Date	[Ethene] ₀	[MP] ₀	[H ₂ O ₂] ₀	[Methanol] ₀	[EG] ₀	Lights (Min)
1	9/25/2023	3129	657	1730	153532	0	2.5
2	9/28/2023	4880	922	1813	158000	0	2.5
3	10/5/2023	0	2804	501	0	0	2
4	10/7/2023	0	2722	624	0	98	2
5	10/8/2023	0	832	1588	78768	24	2
6	10/23/2023	5088	850	1886	155318	0	2

Table B.12: Experimental conditions for experiments with ethene and methylpropene as RO₂ precursors. MP = methylpropene and EG = ethylene glycol.

Exp. No.	Exp. Date	[Ethene] ₀	[B] ₀	[H ₂ O ₂] ₀	[Methanol] ₀	[EG] ₀	Lights (Min)
1	10/09/2023	0	3105	595	0	24	2
2	10/11/2023	0	917	1529	90284	33	2
3	10/26/2023	4320	850	1750	153000	0	2
4	11/1/2023	5088	959	1950	153728	0	2
5	11/5/2023	0	2730	373	0	71	2

Table B.13: Experimental conditions for experiments with ethene and cis-2-butene as RO₂ precursors. B = cis-2-butene and EG = ethylene glycol.

Exp. No.	Exp. Date	[Ethene] ₀	[P] ₀	[H ₂ O ₂] ₀	[Methanol] ₀	[EG] ₀	Lights (Min)
1	2/9/2022	2880	938	1206	990	0	2
2	2/10/2022	2190	3240	1248	1020	0	2
3	2/11/2022	2880	1040	3280	29100	0	2
4	2/14/2022	2920	3240	3167	24300	0	1
5	2/15/2022	2480	1090	3670	24300	0	1

Table B.14: Experimental conditions for experiments with ethene and propene as RO₂ precursors. P = propene and EG = ethylene glycol.

SUPPLEMENTARY INFORMATION FOR CHAPTER 3

C.1 Deuterium Exchange Experiments

To narrow down possible structures for the product at m/z 230 observed during NO_3 -initiated oxidation of furan, we performed a laboratory NO_3 -initiated oxidation experiment in which a chromatogram was performed without deuterium exchange and another was performed with a stream of D_2O intersecting with the effluent of the GC. As can be seen in Figure C.1, the ratio between the signal observed at m/z 231 and the signal observed at m/z 230 does not change across these conditions. We therefore conclude that the compound does not contain an $-\text{OH}$ group or an $-\text{OOH}$ group.

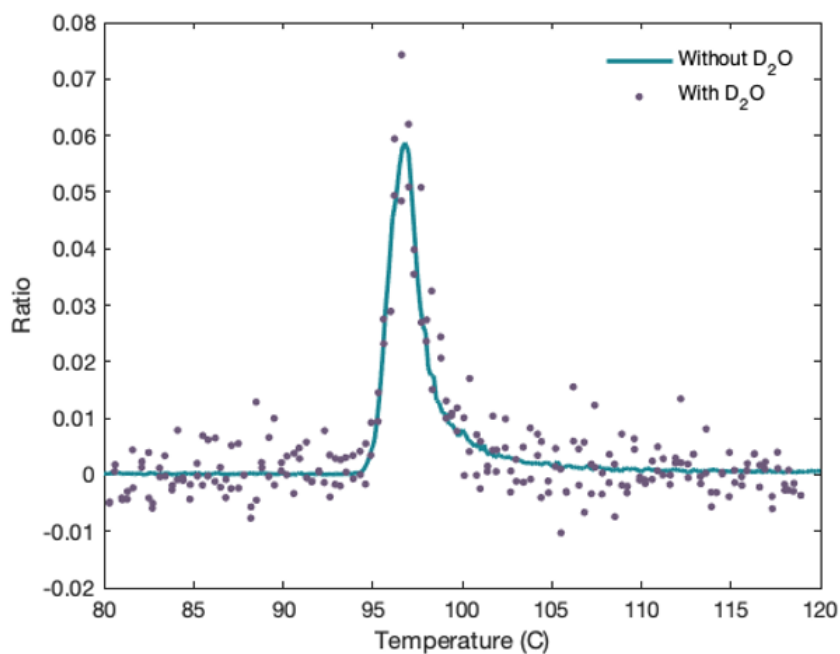


Figure C.1: Comparison between the ratios of the signal at m/z 231 and the signal at m/z 230 during GCs with and without deuterium exchange.

C.2 Additional Results

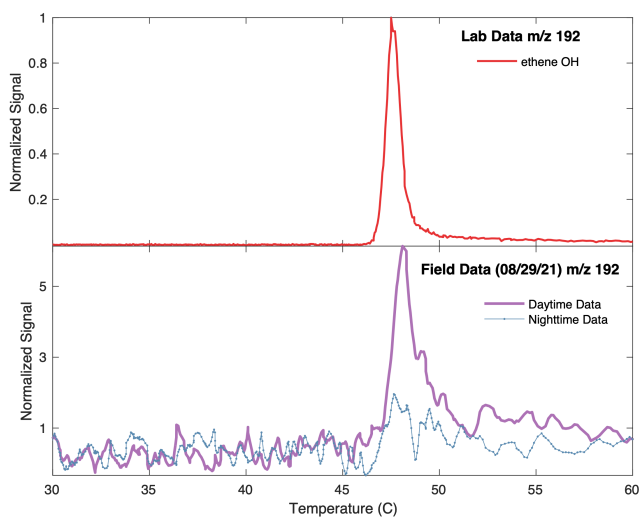


Figure C.2: Sum of ambient chromatograms at m/z 192 taken throughout the day on 08/29/2021 (lower panel), compared with laboratory OH oxidation of ethene. The ambient data is separated into the sum of chromatograms taken during the daytime (purple) and the nighttime (blue).

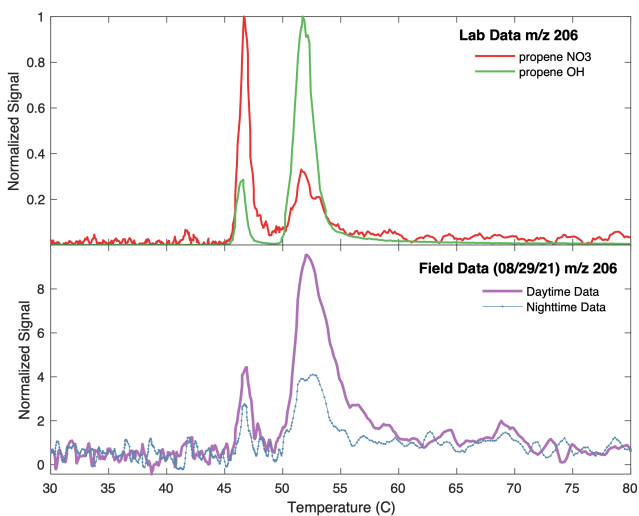


Figure C.3: Sum of ambient chromatograms at m/z 206 taken throughout the day on 08/29/2021 (lower panel), compared with laboratory NO_3 oxidation (red) and laboratory OH oxidation (green) of propene (upper panel). The ambient data is separated into the sum of chromatograms taken during the daytime (purple) and the nighttime (blue).

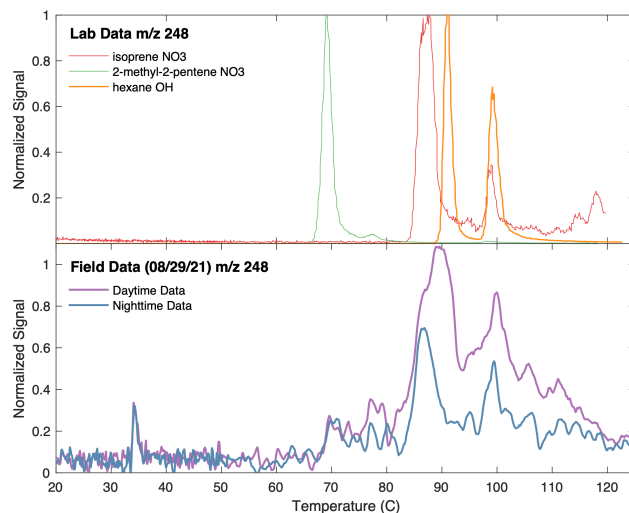


Figure C.4: Sum of ambient chromatograms at m/z 248 taken throughout the day on 08/29/2021 (lower panel), compared with laboratory NO_3 oxidation of isoprene (red) and 2-methyl-2-pentene (green) and the laboratory OH oxidation of hexane (orange) (upper panel). The ambient data is separated into the sum of chromatograms taken during the daytime (purple) and the nighttime (blue).

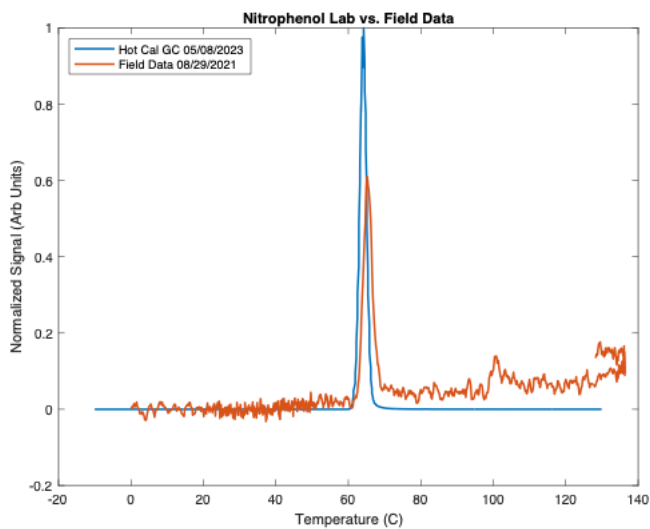


Figure C.5: Sum of ambient chromatograms at m/z 158 taken throughout the day on 08/29/2021 (blue), compared with chromatogram of 2-nitrophenol standard taken in the laboratory (red).

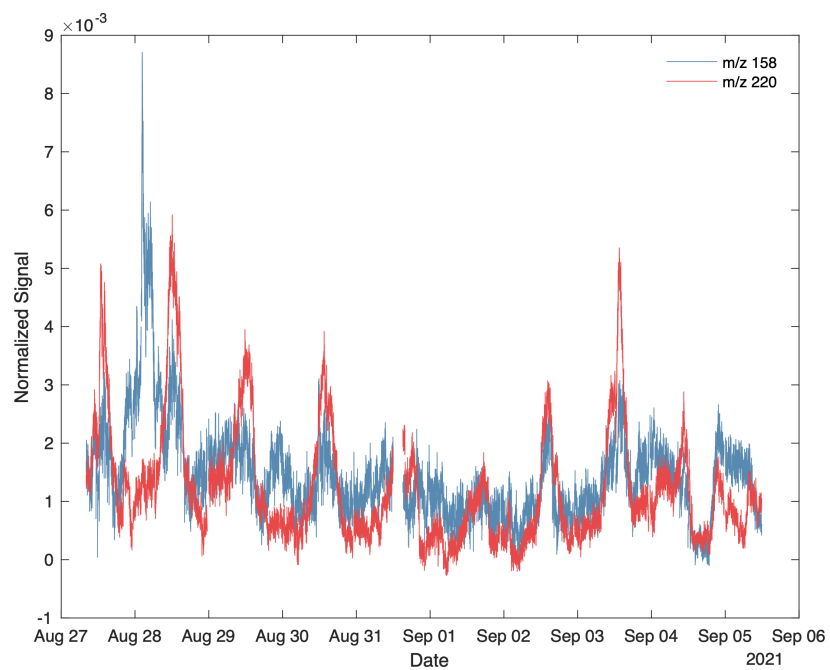


Figure C.6: Comparison between signal observed at m/z 158 and m/z 220 in the CToF-CIMS between August 27th – September 5th.

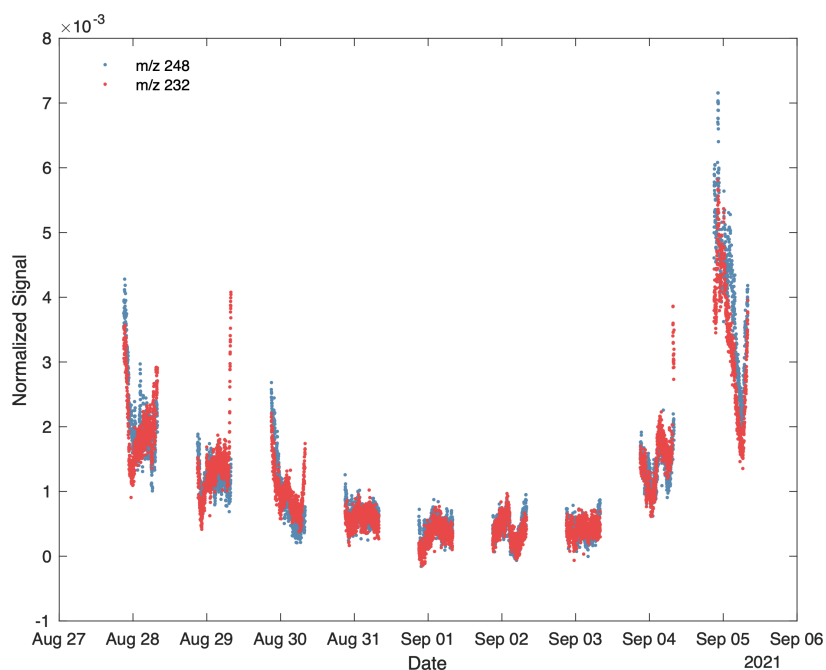


Figure C.7: Comparison between signal observed at m/z 248 and m/z 232 in the CToF-CIMS between August 27th – September 5th at night.

C.3 Isoprene Hydroxy Nitrate Isomer Ratios

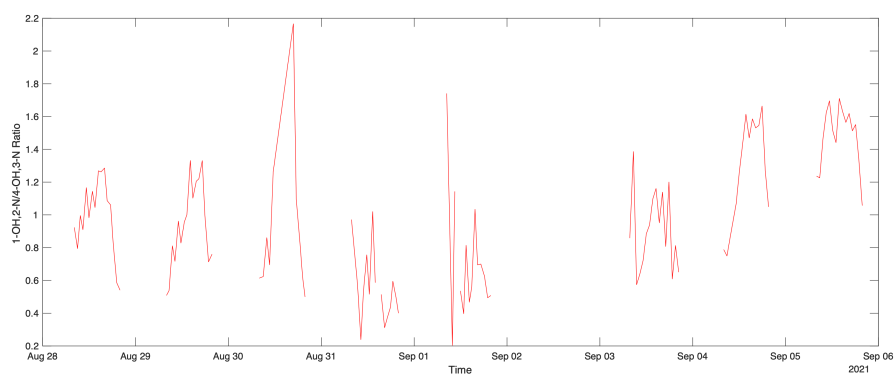


Figure C.8: The ratio of the β hydroxy nitrate isomers throughout the campaign. Data from September 2nd are excluded due to low signals on this day.

C.4 Experimental Conditions and GC Conditions

Date	Hydrocarbon	[HC]	[NO ₂]	[O ₃]	Fraction HC Reacted by NO ₃ /OH/O ₃
5/17/2023	methylpropene	97 (100)	470 (500)	200 (100)	.926/.015/.059
5/18/2023	2-methyl-2-butene	56 (50)	452 (500)	140 (100)	.974/.0046/.022
5/20/2023	isoprene	92.4 (100)	440 (500)	180 (100)	.985/.0026/.012
5/25/2023	2-methyl-1-butene	109 (100)	481 (500)	180 (100)	.974/.0067/.019
5/26/2023	cis-2-butene	56 (50)	692 (700)	116 (100)	.950/.0033/.047
5/26/2023	1,3-butadiene	111 (100)	492 (500)	200 (100)	.984/.0010/.015
5/28/2023	propene	59 (50)	667 (700)	240 (100)	.935/.0034/.062
5/29/2023	isoprene, α -pinene	63 (50), 99 (70)	463 (500)	150 (100)	.959/.011/.030
5/30/2023	2-methyl-2-pentene	56 (50)	455 (500)	210 (100)	.971/.0055/.024
5/30/2023	cis-2-pentene	57 (50)	739 (700)	145 (100)	.948/.0049/.047
5/31/2023	1-butene	63 (50)	700 (652)	211 (100)	.953/.0035/.044
9/8/2023	furan	65 (50)	601 (500)	29 (50)	

Table C.1: Experimental conditions for the ‘dark’ oxidation experiments presented in the analysis of the main body. All concentrations are in ppb. Goal concentrations for each experiment are given in parentheses. The fraction of the relevant hydrocarbon(s) that reacted with each oxidant is estimated by modelling with KinSimPeng and Jimenez, 2019 v. 4.03 in Igor (c/o Danielle Draper) and is given in the final column.

Date	Hydrocarbon(s)	[HC]	[H ₂ O ₂]	[NO]	Oxidation Time (min)
4/24/2023	propene	378	1010	1240	2
	2-methylpropene	61			
	1-pentene	122			
5/3/2023	propene	248	1100	1230	2.1
	ethene	408			
	isoprene	53			
	1-butene	126			
6/26/2023	pentane	554	1100	1230	2.7
7/17/2023	hexane	452	926	1230	5

Table C.2: Experimental conditions for the ‘light’ oxidation experiments that are discussed in the main body. All concentrations are given in ppb.

Date	HC	GC No.	Trap T	Trap Time	Trap Dilution
5/17/2023	methylpropene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	2
		1	-10	2	2
		2	-10	2	6
5/18/2023	2-methyl-2-butene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	1	2
		2	-10	1	6
5/20/2023	isoprene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	1	2
		2	-10	1	6
		3	-10	1	4
5/25/2023	2-methyl-1-butene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	1.8	2
		2	-10	2	6
5/26/2023	cis-2-butene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	1	2
		2	-10	1	4
		3	-10	1	8
5/26/2023	1,3-butadiene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	1.1	2
		2	-10	1	2
5/28/2023	propene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	2	2
		2	-10	2	2
5/29/2023	isoprene, α -pinene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	2	4
		2	-10	2	2

5/30/2023	2-methyl-2-pentene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	1	2
		2	-10	1	6
5/30/2023	cis-2-pentene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	1	2
		2	-10	1	4
5/31/2023	1-butene	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	2	0
		2	-10	2	2
9/8/2023	furan	Zero BG	-10	2	0
		N ₂ O ₅ BG	-10	2	0
		1	-10	1	2
		2	-10	1	6

Table C.3: GC conditions used in the ‘dark’ oxidation experiments. The temperature ramp for all GCs is the same as that used in the collection of the ambient data as given in the main body.

Date	HC	GC No.	Trap T	Trap Time	Trap Dilution
4/24/2023	propene, 2-methylpropene, 1-pentene	BG, 1	-10	2	2
		2	-10	5	2
		3	-10	5	4
5/3/2023	propene, ethene, isoprene, 1-butene	BG, 1, 2	-10	2	4
6/26/2023	pentane	BG	-10	1	6
		1	-10	2	2
7/17/2023	hexane	BG, 1	-10	2	4
		2	-10	6.3	4

Table C.4: GC conditions used in the ‘light’ oxidation experiments. The temperature ramp for all GCs is the same as that used in the collection of the ambient data as given in the main body.

C.5 CIMS Sensitivities

Compound	Sensitivity
Isoprene hydroxy nitrate	3.5×10^{-4}
C4 hydroxy nitrates	3.4×10^{-4}
Propene hydroxy nitrates	5.0×10^{-4}
Isoprene carbonyl nitrates	3.6×10^{-4}
Otherwise	3.5×10^{-4}

Table C.5: CToF sensitivities used in the analysis presented in Chapter 3. All sensitivities are the same as those used in Vasquez, Allen, et al., 2018.

C.6 Bootstrap Bet Fits of Ambient Data

Bootstrap best fits of the sums of daytime and nighttime ambient chromatographic data were performed for m/z 230 and m/z 234 using a modified . At m/z 230, all five peaks were fit. The two latest eluting peaks were fit separately, while the three earliest eluting peaks were fit either together or separately, depending on the resolution of the chromatogram. The percent contribution of each peak was then determined by summing all of the fitted areas to obtain the total area. Figure C.9 gives the average contributions during the daytime and nighttime of the isoprene and furan-derived products as determined by these fits. At m/z 234, only the 4-5 latest eluting peaks were fit in order to determine the contribution of the MVK/MACR-derived nitrates to the overall signal at m/z 234. The overall GC signal at m/z 234 was determined by applying the baseline used in the individual peakfits and then summing over the entire signal. Below are the results of the peakfits that were used in each case. In some cases, a daytime or nighttime fit was not performed due to poor signal-to-noise ratios. In the table below, NT = nighttime and DT = daytime.

Date (Time)	Position	Width	Area	Error	R ²
08/28/21 (DT)	[845.9 913.7 925.2]	[14.52 10.25 8.78]	[0.063 0.12 0.65]	2.95%	0.98
08/28/21 (NT)	[845.6 912.8 924.8]	[10.70 11.03 7.90]	[0.064 0.17 0.25]	4.28%	0.97
08/29/21 (DT)	[846.1 912.5 924.9]	[9.71 10.20 8.21]	[0.0071 0.059 0.37]	3.30%	0.98
08/29/21 (NT)	[847.0 912.2 924.3]	[11.32 10.45 7.98]	[0.12 0.33 0.71]	3.43%	0.98
08/30/21 (DT)	[845.9 913.5 924.2]	[5.85 10.09 9.11]	[0.0070 0.027 0.16]	3.39%	0.97
08/30/21 (NT)	[846.1 912.6 925.5]	[9.84 12.11 7.55]	[0.082 0.23 0.38]	3.76%	0.97
08/31/21 (DT)	[845.7 912.8 924.2]	[18.85 7.83 9.12]	[0.027 0.043 0.35]	3.10%	0.98
08/31/21 (NT)	[846.7 912.1 925.3]	[16.63 8.05 9.70]	[0.028 0.079 0.41]	4.13%	0.96
09/01/21 (DT)	[845.6 915.6 927.2]	[20.0 5.39 7.62]	[0.0067 0.024 0.14]	5.51%	0.93
09/01/21 (NT)	[846.9 914.2 927.6]	[11.92 8.86 11.79]	[0.042 0.083 0.45]	3.81%	0.97
09/02/21 (NT)	[846.0 916.0 927.1]	[16.42 14.31 7.59]	[0.045 0.16 0.23]	4.65%	0.96
09/03/21 (DT)	[846.8 913.8 925.6]	[13.51 9.59 9.58]	[0.052 0.099 0.40]	3.97%	0.97
09/03/21 (NT)	[845.2 912.8 926.3]	[10.06 9.41 9.96]	[0.23 0.40 0.86]	3.72%	0.97
09/04/21 (DT)	[845.6 912.3 926.1]	[14.35 5.69 12.79]	[0.052 0.067 0.31]	5.30%	0.95
09/04/21 (NT)	[845.6 861.8 912.9 924.2]	[10.0 10.0 10.0 10.0]	[0.43 0.18 1.35 0.87]	10.88%	0.84
09/05/21 (DT)	[846.7 912.5 926.1]	[16.49 10.69 8.16]	[0.13 0.40 0.45]	4.01%	0.97
09/05/21 (NT)	[845.5 912.7 925.8]	[11.15 8.39 10.93]	[0.16 0.33 1.06]	4.12%	0.97

Table C.6: Bootstrap best fit results for GC peaks observed in the ambient data at m/z 230 during the RECAP-CA campaign between 08/28/2021 – 09/05/2021. Peak position is given as elution time in seconds, and peak width is given in seconds.

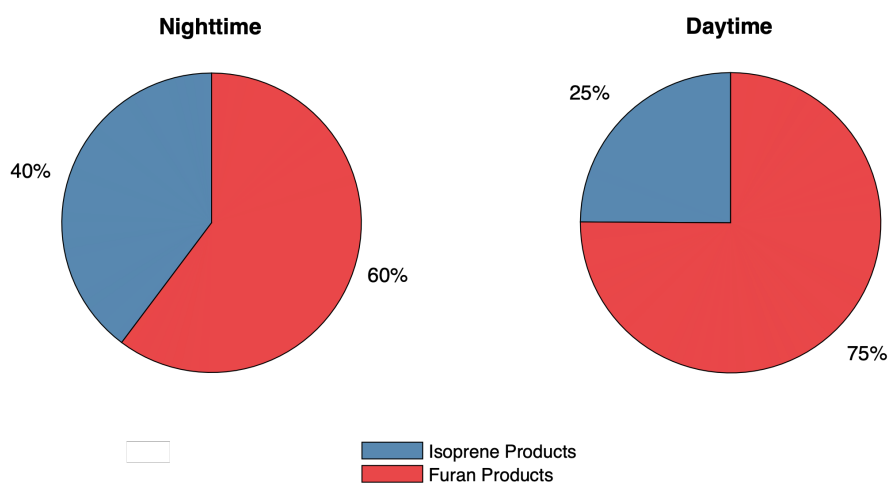


Figure C.9: Average contributions of isoprene and furan-derived products at m/z 230 between 08/28/2021 – 09/05/2021 during the daytime and nighttime. Percent contributions are determined from the results of the best fits given in Table C.6.

Date (Time)	Position	Width	Area	Error	R ²	Total Area
08/28/21 (DT)	[903.5 920.5	[10.0 8.67	[0.20 0.36	2.84%	0.98	1.47
	940 982.6]	10.0 10.0]	0.055 0.31]			
08/28/21 (NT)	[902.5 920.9	[10.0 10.0	[0.011 0.012	11.26%	0.74	0.12
	938.2 981.6]	4.53 6.69]	0.0061 0.016]			
08/29/21 (DT)	[902.6 919.0	[8.27 9.31	[0.11 0.47	2.37%	0.99	1.29
	934.7 982.7]	10.0 10.0]	0.0037 0.36]			
08/29/21 (NT)	[901.9 918.5	[10.0 6.7	[0.030 0.034	6.78%	0.90	0.42
	935.6 980.7]	10.0 10.0]	0.027 0.054]			
08/30/21 (DT)	[901.1 918.5	[10.0 7.51	[0.026 0.046	5.15%	0.93	0.19
	936.6 979.6]	8.40 10.0]	0.020 0.031]			
08/30/21 (NT)	[902.2 919.7	[10.0 9.4	[0.018 0.033	9.97%	0.73	0.41
	937.9 980.2]	6.9 9.3]	0.023 0.044]			
08/31/21 (DT)	[901.4 919.4	[10.0 10.0	[0.098 0.098	5.65%	0.94	0.59
	936.2 980.9]	9.8 9.5]	0.057 0.053]			
09/01/21 (DT)	[904.3 921.5	[10.0 10.0	[0.065 0.089	5.04%	0.96	0.38
	938.6 984.8]	9.28 10.0]	0.022 0.068]			
09/02/21 (DT)	[904.2 920.4	[8.7 10.0	[0.062 0.14	6.09%	0.92	0.63
	938.8 985]	10.0 10.0]	0.039 0.14]			
09/03/21 (DT)	[903.4 920.1	[10.0 8.9	[0.18 0.40	2.86%	0.99	1.39
	938.4 984.7]	10.0 10.0]	0.015 0.41]			
09/03/21 (NT)	[905 921.7	[7.0 10.0	[0.027 0.059	6.04%	0.90	0.57
	940 984.7]	10.0 7.7]	0.0051 0.031]			
09/04/21 (DT)	[905.4 922.7	[4.6 12.4	[0.025 0.25	2.97%	0.99	0.84
	942.6 988.7]	4.0 14.2]	0.010 0.25]			
09/04/21 (NT)	[905.7 919.1	[10.0 9.8	[0.017 0.098	5.10%	0.94	0.30
	935.3 985.4]	2.17 9.31]	0.0069 0.076]			
09/05/21 (DT)	[904.5 922.1	[9.6 11.2	[0.058 0.48	4.66%	0.97	2.01
	941.1 987.9]	4.5 12.2]	0.012 0.60]			

Table C.7: Bootstrap best fit results for GC peaks observed in the ambient data at m/z 234 above 85°C between 08/28/2021 – 09/05/2021. Peak position is given as elution time in seconds, and peak width is given in seconds.

*Appendix D***BRINGING A LENS OF EQUITY TO GEOSCIENCE
QUALIFYING EXAMINATIONS**

This manuscript, written and developed with Clare E. Singer and Lilian A. Dove, was the culmination of several years of work through our graduate school careers aimed at probing the equity of qualifying examinations in the Geological and Planetary Sciences (GPS) division at Caltech and working to redesign these exams in a more equitable manner. Additional information about this work can be found in the appendices of Singer, 2024 and Dove, 2023.

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AGU Advances

COMMENTARY

10.1029/2024AV001260

Peer Review The peer review history for this article is available as a PDF in the Supporting Information.

Key Points:

- Qualifying exams in the geosciences are an understudied yet potentially important failure point for retention of underrepresented students
- The design and implementation of the qualifying exam should be done in a data-driven and iterative way to ensure equity in outcomes
- Graduate programs should be specific in their definition and communication of a successful exam outcome with students

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

L. A. Dove,
dove@brown.edu

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Author Contributions:

Conceptualization: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Formal analysis: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Investigation: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Resources: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Visualization: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Writing – original draft: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Writing – review & editing: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Writing – review & editing: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Writing – review & editing: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Writing – review & editing: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

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Writing – review & editing: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Writing – review & editing: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Writing – review & editing: Lilian A. Dove, Clare E. Singer, Sara E. Murphy

Bringing a Lens of Equity to Geoscience Qualifying Examinations

Lilian A. Dove^{1,2} , Clare E. Singer^{1,3} , and Sara E. Murphy⁴ 

¹Cooperative Programs for the Advancement of Earth System Science, University Corporation for Atmospheric Research, Boulder, CO, USA, ²Department of Earth, Environmental and Planetary Sciences, Brown University, Providence, RI, USA, ³Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY, USA, ⁴Department of Environmental Science and Engineering, California Institute of Technology, Pasadena, CA, USA

Abstract Qualifying examinations are an important milestone in geoscience graduate programs, but students with marginalized identities are disproportionately lost from graduate programs around the time of these exams. Inequity in qualifying exams can enter at multiple stages throughout the exam design, student mentorship experience, exam administration, and post exam feedback. Therefore, robust assessment is necessary when building an equitable examination. We provide concrete suggestions for graduate programs to evaluate and modify their qualifying examinations. The data-driven and iterative process encourages graduate programs to outline specific expectations for success, employ best-practice pedagogy, proactively support students, and use data to measure progress and inform changes in the examination.

Plain Language Summary In most geoscience graduate programs, students are required to pass a qualifying examination to demonstrate their ability to successfully complete a PhD. These examinations vary in structure and content across programs. However, there are often concerns over the value and equity of these examinations. In this paper, we provide an outline of concrete steps geoscience graduate programs can take to begin ensuring that the outcomes and experiences students have with the qualifying examination are equitable. The recommendations span many aspects of the exam including the design, support for students preceding the exam, administration of the exam itself, and feedback and assessment activities after the exam. Most importantly, the proposed process is iterative and data-driven, meaning that graduate programs can continually refine and make changes to qualifying examinations based on outcomes and experiences.

1. Introduction

A majority of geoscience graduate programs have qualifying examinations that seek to assess a student's progress and ability to successfully complete their degree (Harshman, 2021; Leshner & Scherer, 2018). These examinations can be a valuable and important milestone for graduate students (Baker & Pifer, 2011; McAdams III et al., 2013). However, they can additionally be a point at which students, particularly those with identities marginalized in science, are lost from or leave degree-granting programs (Till, 2023; Wilson et al., 2018), contributing to the “hostile obstacle course” of academia (Berhe et al., 2022; Liera et al., 2023) and impacting student health and well-being (DiPietro et al., 2010; Furstenberg & Nichols-Casebolt, 2001; Lopez, 2022). We use “qualifying exam” as a general term to refer to any milestone exam in a graduate program which must be passed to continue toward the degree completion, although these examinations go by different names.

Statistical biases in the pass rates of these qualifying exams highlight their potential discriminatory nature. In several graduate programs in the United States, including geoscience programs, students who identify as women are disproportionately more likely to fail their qualifying examinations than male-identifying students (Kurfess et al., 2020; Singer, 2024; Till, 2023). Other programs have noted differences between the experiences of domestic and international students (Hestenes et al., 2022; Santiago & Nguyen, 2020). Unfortunately, for many programs, limited to no data exists on differences in outcomes by gender identity, race, citizenship status, LGBTQ+ identity, first-generation student status, or many other identity axes. This is a result of either a lack of data collection (McLaughlin et al., 2023) and/or statistically small sample sizes of underrepresented groups. As the geosciences are one of the least racially diverse scientific fields (Bernard & Cooperdock, 2018; Dutt, 2020), and women, non-binary people, and disabled people remain underrepresented in certain geoscience subfields (Gonzalez, 2009; Ranganathan et al., 2021), it is vital that geoscience graduate programs assess their qualifying examinations as a potential point of failure of the academe for marginalized groups.

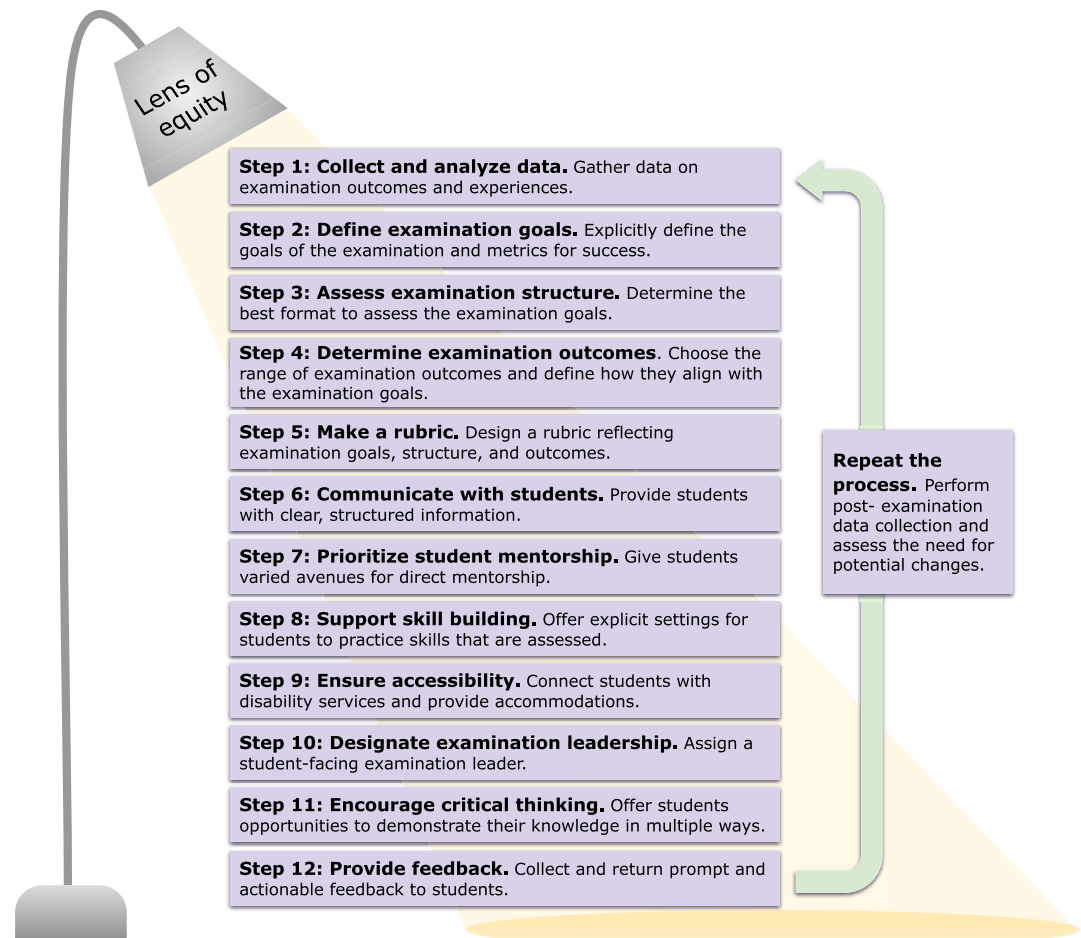


Figure 1. Steps to foster more equitable qualifying examinations in geoscience. In this data-driven, iterative process, a graduate program uses data to inform changes in the examination; provides specific and explicit expectations for success; employs best-practice pedagogical standards; proactively provides student support; and uses data to measure progress.

To best serve the geoscience community, qualifying examinations must be undertaken and assessed through a lens of equity (McLaughlin et al., 2023). It is vital to consider the messaging and resources provided to students before, during, and after the examination as sources of inequity. While the administration of the exam itself is a place where implicit bias may enter, other activities surrounding the exam can also be sources of inequity—from its design, support and communication leading up to the exam, and feedback after the exam. We present a collection of concrete recommendations aimed at making qualifying examinations more equitable and propose a framework that is transferable across geoscience graduate programs (Figure 1). While suggestions are outlined here, further information around many steps are outlined in Supporting Information S1.

2. Framework for Fostering More Equitable Qualifying Examinations

2.1. Step 1: Collect and Analyze Data. Gather Data on Examination Outcomes and Experiences and Assess the Need for Changes

As in natural science, the first step in assessing an examination's success is gathering the relevant data (Ali et al., 2021; Avery et al., 2022; Ormand et al., 2022). Graduate programs should collect quantitative data on examination outcomes alongside information on student identities and the intersections thereof (Ali et al., 2021; Núñez et al., 2020). Where possible, historical data should be gathered and synthesized. Data should be made public within the graduate department, following any institutional regulations, anonymizing and redacting data that identifies individuals, and allowing for self-description of identity (Myanna, 2023). In order to maintain

anonymity in the case of small numbers of students from specific groups (e.g., racial identity (Bernard & Cooperdock, 2018) or fields of study), data can be aggregated over several years.

In addition to the quantitative data on examination outcomes with respect to identity, graduate programs should also collect qualitative data on students' experiences with the examination (Memarian et al., 2019), through processes like anonymous surveys (see Supporting Information S1 for example questions). Department or campus climate surveys provide the opportunity to collect this data in the context of other aspects of the program. This qualitative feedback from students is vital to assess whether students have productive learning experiences before, during, and after the qualifying examination. While the quantitative data on examination outcomes is necessary, the student experience data provides a more holistic view to ensure that programs are meeting their equity goals and that the exam is functioning as a learning experience for students.

Programs should take time to consider metrics for what constitutes a successful exam when evaluating the data on outcomes and experiences. Examples of such metrics may be a certain pass rate, equity in pass rates between identity groups, achieving certain thresholds of high-quality mentorship as reported by students, or thresholds for actionable feedback. Defining these metrics at the outset will help the program both design and analyze their surveys. Examples of data that can spark concern for inequity in a qualifying exam include statistically significant differences in pass rates for students of different identity groups, for example, men, women, and non-binary individuals, or native English speakers and non-native English speakers. Furthermore, students expressing inadequate preparation or mentorship leading up to the exam or sparse feedback after the exam are causes for concern and highlight potential intervention points.

2.2. Step 2: Define Examination Goals. Explicitly Define the Goals of the Examination and Metrics of Success

To achieve evidence-based best practices, graduate programs must consolidate a definition of success that examiners use to decide examination outcomes (see Supporting Information S1 for examples) (Furstenberg & Nichols-Casebolt, 2001; Posselt & Liera, 2022). These criteria for success should rise above individual perceptions (Kostohryz, 2016) and the concept of the qualifying examination as a historically necessary “hurdle” (Posselt et al., 2021) or “rite of passage” (Estrem & Lucas, 2003). Although subjectivity is inherent in their design (Liera et al., 2023), being specific in what outcomes are and are not acceptable for a successful examination can help reduce this subjectivity.

Without a clear and unified statement about the goals of the examination from the degree program, faculty and students can derive different views of the examination's purposes (Guloy et al., 2020) and examinations may carry examiners' implicit biases or unwritten expectations (MacLachlan, 2017). In addition, vagueness in expectations significantly increases student stress and anxiety, which can impact examination performance (Andrade & Du, 2019; DiPietro et al., 2010; Harding-DeKam et al., 2012). By explicitly defining what success looks like and how students can achieve that goal, graduate programs ensure that students can focus on putting their time into building skills that will be assessed, rather than focusing on things that are not being examined. For instance, if a student's oral presentation skills are (or are not) part of the assessment, this can be explicitly stated so students know whether they should put time into practicing their presentations. In a field as broad as the geosciences, which covers topics across the biosphere, hydrosphere, cryosphere, atmosphere, and geosphere, programs must be explicit about what topics students must be versed in for a successful outcome.

2.3. Step 3: Assess Examination Structure. Determine the Best Format to Assess the Examination Goals

There are a range of structures of qualifying examinations across graduate programs, including written examinations, oral examinations, or a combination of formats. There are benefits and drawbacks to each of these structures that are typically dependent on the goals of the graduate program and the required coursework. In addition, qualifying examinations can also occur at a range of times in a graduate program. Programs must assess if the structure of the qualifying examination is a remnant of tradition or if it truly fits the goals of the examination outlined in Step 2, particularly as informed by student feedback detailed in Step 1 (Allard et al., 2021). A range of potential structures are described in the Supporting Information S1.

2.4. Step 4: Determine Examination Outcomes. Choose the Range of Examination Outcomes and Define How They Align With the Examination Goals

Programs should additionally consider the potential outcomes of a qualifying examination. While a stark pass/fail option may be the most straightforward, offering a “conditional pass” can help the exam serve its purpose as a learning opportunity. The use of a conditional pass result requires examiners to identify the cause of the concern and to specify the conditions to be met for the student to pass (Wilkinson et al., 2011). Under a conditional pass, students may be required to take, retake, or be a teaching assistant for a certain class, or do individual study under faculty guidance.

2.5. Step 5: Make a Rubric. Design a Rubric That Reflects the Examination Goals, Structure, and Outcomes

Rubrics are a fundamental tool for providing information to students on areas of assessment and for programs to assess preparation of students along different axes (Cockett & Jackson, 2018; Wolf & Stevens, 2007) (see Supporting Information S1 for examples). The effective use of rubrics provides consistent assessment through reproducible scoring, reducing subjectivity inherent to qualifying examinations (Science Education Resource Center, 2024). It is important to note that rubrics do not inherently imply inflexibility in exam content; rubrics can be adaptable to individual examinations, with examiners filling in topics on the rubric specific to an individual students' examination. In the case of a rubric which is adapted to individual examinations, the rubric may initially be a somewhat sparse document, but should still outline the assessed skills. Well in advance of the examination, examiners should explain the rubric to the students, as students who understand a rubric are more likely to have greater assessment performance outcomes (Francis, 2018). The rubric must be detailed enough to usefully inform the examination outcome (Brookhart & Chen, 2015).

2.6. Step 6: Communicate With Students. Provide Students With Clear, Structured Information

Steps 2–5 are incomplete without clearly communicating the information to students. The goals, rubric, and possible outcomes of the exam should be carefully explained, both in writing and verbally, with ample opportunity for students to ask questions provided. Graduate programs may hesitate to provide transparency on the examination in an effort to increase flexibility; however, transparency and flexibility are not mutually exclusive. Even, or especially, in situations where the exam is highly individualized, the program should communicate this flexibility clearly to the students. It is important that students receive official information from the program rather than potentially haphazard information from other sources. Students may also have financial, immigration, or personal concerns related to examination outcome that can be addressed with transparent communication from the graduate program. The production and explanation of a definition of examination success and a rubric (Step 5) is a concrete step to providing this information to students.

2.7. Step 7: Prioritize Student Mentorship. Give Students Varied Avenues for Direct Mentorship

Clear communication between students and faculty is a requisite for student success at all stages. Therefore, it is necessary to ensure students receive quality faculty mentorship throughout the time leading up to the examination, as the success and satisfaction of graduate students is closely tied to their mentorship experience (Paglis et al., 2006; Tuma et al., 2021). This practice is especially important for historically excluded groups, as these students are more likely to struggle to find supportive mentors (National Academies of Sciences, Engineering, and Medicine; Policy and Global Affairs; Board on Higher Education and Workforce; Committee on Effective Mentoring in STEMM, 2019a). In particular, peer and cross-institutional mentoring programs have been demonstrated to enhance the success of underrepresented groups in the biomedical sciences (Wilson et al., 2018) and the geosciences (Huntoon et al., 2015).

Advisors and faculty mentors should frequently engage in open communication with their mentees about their needs, including developing a timeline for progress leading up the examination and a discussing the required support to reach the outlined goals, in line with mentorship best practices (National Academies of Sciences, Engineering, and Medicine; Policy and Global Affairs; Board on Higher Education and Workforce; Committee on Effective Mentoring in STEMM, 2019b). Examples of mentorship best practices in the Supporting Information S1, but frequent student surveys are an excellent way to evaluate whether students are receiving quality mentorship.

2.8. Step 8: Support Skill Building. Offer Explicit Settings for Students to Practice the Skills That Will Be Assessed

Students must be provided both structured and unstructured environments to practice skills assessed during the exam (examples in the Supporting Information S1). Such intervention was shown to be successful in combating attrition of historically marginalized students in the biomedical sciences (Wilson et al., 2018) and increasing students' self-efficacy in the geosciences (Baber et al., 2010). Formative opportunities for students to demonstrate knowledge under minimal test anxiety was also shown to increase performance on high-stakes exams, particularly for women (Ballen et al., 2017; Cotner & Ballen, 2017; Salehi et al., 2019).

Vitally, students must be provided feedback on their practice, preferably using the rubric developed for the qualifying examination (Johnson et al., 2016; Morris et al., 2021). This provides students the ability to mentally align their actions with their outcomes in a lower-stakes environment (Rose et al., 2006) and also gives examiners practice applying the rubric. Students should have several points of contact from whom they can receive feedback, and care must be taken to ensure that historically marginalized students are not excluded from informal mentoring circles (Liera et al., 2023).

2.9. Step 9: Ensure Accessibility. Connect Students With Disability Services and Provide Accommodations

Upwards of 13% of the United States population is disabled, but disabled students are regularly underrepresented in and not served fully by graduate programs (Brown & Leigh, 2018; Dali, 2018). There is an additional discrepancy in geoscience graduate programs, as geoscience has a reputation for being unfriendly for disabled students due to its historical reliance on often inaccessible field data (Atchison & Libarkin, 2016; Lawrence, 2021; Mol & Atchison, 2019).

Qualifying examinations can present an additional barrier for disabled students. For instance, examinations that are several hours long may not be accessible for students with learning or physical disabilities, the examination room may not be appropriate for students with sensory processing disorders, or accessibility technology may need to be adapted for an examination's format. Graduate programs should provide the university's accessibility and disability services program information on the examination format and proactively provide all students with information about how to connect with and attain accommodations through these offices well in advance of the examination date. Graduate programs must follow through to provide necessary accommodations for students.

2.10. Step 10: Designate Examination Leadership. Assign a Student-Facing Examination Leader

During the exam it is important to have a designated examination leader who can advocate for the student and answer any questions that arise (more details in Supporting Information S1). This person should be available during the exam, but also ahead of the exam, to answer questions. This role is applicable across multiple exam formats. In particular, this student-facing examiner should monitor examiner behavior and enact bystander intervention steps in the case of questioning that is out of scope or hostile (Haynes-Baratz et al., 2021; Shea et al., 2019). This role is vital, as antagonistic and demeaning environments and interactions are one major reason that students may leave the geosciences (Cabay et al., 2018; Marín-Spiotta et al., 2020).

2.11. Step 11: Encourage Critical Thinking. Offer Students Opportunities to Demonstrate Their Knowledge in Multiple Ways

Often, one of the primary goals of qualifying examinations is to assess students' abilities to make connections between topics and engage with questions that require complex thinking. Offering opportunities for students to participate in diverse ways to effectively express their knowledge is a key component of inclusive instructional design (Capp, 2017; Carabajal et al., 2017). For example, the exam can provide both written and oral formats for students to share the same knowledge. Students can be provided with paper or a whiteboard during an oral exam to write down thoughts or explanations. Or students can be prompted to explain their answers in diverse ways using metaphors, pictures, equations, data, or more. Examiners should encourage students to use these alternative methods and provide alternative ways to engage with the questions (Abegglen et al., 2021; Rose et al., 2006) through prompting questions or availability of tools.

2.12. Step 12: Provide Feedback. Collect and Return Prompt and Actionable Feedback to Students

A key part of treating qualifying examinations as a learning experience is providing students feedback on their performance so they can reflect on their successes and be made aware of places for improvement (Haughney et al., 2020; Jensen et al., 2012; Poulos & Mahony, 2008). Feedback can focus on both topics where students performed well and topics where students can improve. In all cases, feedback must focus on the student's performance on the examination, not on a student's personal characteristics or the examiner's perception of the student's belonging in academia. Feedback should be actionable, meaning that students should walk away with a specific understanding of where and how they can improve.

In the case where students are asked to retake an examination, prompt and actionable feedback presents students the ability to focus their attention on places where they can improve (Evans, 2013). In the case where students passed an examination, prompt and actionable feedback provides a confidence boost and also gives students goals to focus on for the future. Strategies for providing cohesive feedback are detailed in the Supporting Information S1.

3. Conclusion

Graduate programs should conduct a regular, data-informed review of their qualifying exam, using a lens of equity to ensure that student outcomes and experiences are equitable across identity groups. The framework we have outlined above must be approached iteratively, using the quantitative and qualitative data collected to inform and assess changes made to the examination. Data analysis and examination updates do not need to necessarily be repeated every year, but should align with the frequency and nature of changes made to the exam. Patterns in outcomes and experiences may take time to emerge, particularly in small programs. However, regularly scheduled evaluations of outcomes are vital to assess progress, achievement, and maintenance of equitable examination outcomes (Ruggs & Avery, 2021) and student support.

Qualifying examinations are an understudied yet potentially important place where students underrepresented in the field are not retained. Geoscience graduate programs can address this challenge by being mindful about their examination practices and approaching their creation, execution, and assessment through a lens of equity. By addressing this issue with evidence-based practices, geoscience graduate programs can align their values with their actions, enhance the graduate student experience, and pursue equity in the scientific endeavor.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data were not used, nor created for this research.

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