

**Investigating sources and sinks of organic aerosol:  
NO<sub>3</sub>-initiated oxidation of isoprene and  
heterogeneous oxidation of organic aerosol**

Thesis by

Alan J. Kwan

In Partial Fulfillment of the Requirements for the degree of

Doctor of Philosophy



CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

2011

© 2011

Alan J. Kwan

All Rights Reserved

## Acknowledgments

While only my name appears on the front of this work, it is the result of a collective effort studying a complex system, one involving instrumental development, laboratory and field studies, data analysis, and – as in many human experiences – tedium and drama, frustration and elation. I am honored to have navigated the scientific challenges and emotional vicissitudes with the support of a great team of collaborators and friends.

A constant force in the development of this work has been the intellectual vibrancy of Paul Wennberg and his group. In addition to Paul, John Crouse, David McCabe, Andreas Kürten, Jason St. Clair, Fabien Paulot, Nathan Eddingsaas, Melinda Beaver, and Coleen Roehl provided essential guidance on countless aspects of this work, although the support and encouragement of group members with whom I did not directly collaborate has been invaluable as well.

The Wennberg group's blatant ignorance of boundaries led me to collaborate with John Seinfeld, Richard Flagan, and their group at the Caltech environmental chamber. Here, Jesse Kroll, Nga Lee (Sally) Ng, Arthur Chan, Jason Surratt, Man Nin Chan, Puneet Chhabra, Shane Murphy, Armin Sorooshian, Scott Hersey, Havala Pye, Beth Kautzman, Lindsay Yee, and Christine Loza broadened my perspectives by introducing me to the practices of aerosol science and integrating me into their tight-knit community.

Outside of these two groups, I am also indebted to Janet Hering and Jared Leadbetter, who provided me with initial laboratory experience during my first year as a graduate student, Nathan Dalleska, who informed me with his analytical expertise, Rick Gerhardt, the glassblower who fixed many of my mistakes, and Rick Paniagua and his

team at the Physics machine shop, who taught me about the design and construction of the custom components that make much of this work possible. Outside of Caltech, I am also grateful for the opportunities to do field work sponsored by the National Aeronautics and Space Administration (NASA) and the National Oceanic and Atmospheric Administration (NOAA), which exposed me to different techniques and perspectives in atmospheric chemistry; my coauthors on Chapter 4 were especially helpful, but there are many other investigators whom I met during these missions and subsequent science team meetings who were generous with their time and knowledge to help me gain a foothold in a complicated field. Finally, my outside committee members, Mitchio Okumura and Alex Sessions, also deserve recognition for taking time out of their work to lend their fresh perspectives onto mine.

Lastly, this work is the result of efforts of many strangers, some recognized as Carlylian giants though most consigned to anonymity by history, whose struggles and ultimate successes have allowed me to live in an age and a place where living past one's 30<sup>th</sup> birthday is commonplace, and where I have the freedom to pursue my own dreams and make my own mistakes. Many in this world and in history have not shared my good fortune, often through no fault of their own. Regardless of this work's ultimate impact, I should be thankful that I had the opportunity to pursue it.

Brief mentions don't do justice to everyone's contributions, and I have likely neglected to mention many. Any omissions in acknowledgments, as well as any errors contained in the work that follows, are entirely my fault.

## Abstract

Secondary organic aerosol (SOA) are important components in atmospheric processes and significantly impact human health. The complexity of SOA composition and formation processes has hampered efforts to fully characterize their impacts, and to predict how those impacts will be affected by changes in climate and human activity. Here, we explore SOA formation in the laboratory by coupling an environmental chamber with a suite of analytical tools, including a gas-phase mass spectrometry technique that is well suited for tracking the hydrocarbon oxidation processes that drive SOA formation. Focusing on the oxidation of isoprene by the nitrate radical,  $\text{NO}_3$ , we find that reactions of peroxy radicals ( $\text{RO}_2$ ) to form ROOR dimers is an important process in SOA formation. The other gas-phase products of these  $\text{RO}_2$  reactions differ from what is expected from studies of simpler radicals, indicating that more studies are necessary to fully constrain  $\text{RO}_2$  chemistry. Finally, we examine the role of heterogeneous oxidation as a sink of organic aerosol and a source of oxygenated volatile organic compounds in the free troposphere.

## Table of Contents

|   |     |
|---|-----|
| Acknowledgments   | iii |
| Abstract  | v   |
| <b>Chapter 1: Introduction</b>  | 1   |
| References  | 6   |
| <b>Chapter 2: Secondary organic aerosol formation from the reaction of<br/>isoprene with nitrate radicals</b> | 15  |
| Abstract  | 16  |
| 2.1 Introduction  | 16  |
| 2.2 Experimental  | 19  |
| 2.3 Results   | 24  |
| 2.3.1 Blank experiments   | 24  |
| 2.3.2 Aerosol yields  | 25  |
| 2.3.3 Gas-phase measurements  | 27  |
| 2.3.4 Chemical composition of SOA   | 30  |
| 2.3.4.1 Aerosol Mass Spectrometer (Q-AMS)<br>measurements   | 30  |
| 2.3.4.2 Offline chemical analysis   | 31  |
| 2.4 Gas-phase chemistry and SOA formation   | 34  |
| 2.4.1 Formation of various gas-phase products   | 34  |
| 2.4.2 Effect of peroxy radical chemistry on SOA yield   | 37  |
| 2.4.3 Growth curves: multiple steps in SOA formation  | 39  |
| 2.4.4 Proposed mechanisms of SOA formation  | 41  |

|  |   |     |
|--|---|-----|
| 2.5  | Approximate estimate of global SOA production from isoprene + NO <sub>3</sub> | 48  |
| 2.6  | Implications  | 51  |
|  | Acknowledgments   | 54  |
|  | References  | 55  |
|  | Tables  | 72  |
|  | Figures   | 80  |
| <br>   |   |     |
| <b>Chapter 3: Products of peroxy radical reactions from the NO<sub>3</sub>-initiated oxidation of isoprene</b> |   |     |
|  | <b>Abstract</b>   | 98  |
|  | <b>Abstract</b>   | 99  |
| 3.1  | Introduction  | 99  |
| 3.2  | Experimental  | 102 |
| 3.3  | Results and Discussion  | 105 |
| 3.3.1  | Nitrate yield   | 106 |
| 3.3.2  | Hydroxyl radical (OH) formation   | 109 |
| 3.3.3  | RO <sub>2</sub> -RO <sub>2</sub> branching ratio                              | 114 |
| 3.3.4  | RO radical fate and HO <sub>2</sub> production                                | 116 |
| 3.3.5  | Formation of dimer compounds  | 117 |
| 3.4  | Implications  | 118 |
|  | Acknowledgments   | 124 |
|  | References  | 124 |

|  |     |
|--|-----|
| Tables   | 148 |
| Figures  | 150 |
| <b>Chapter 4: The potential flux of oxygenated volatile organic compounds from organic aerosol oxidation</b> |     |
| <b>Abstract</b>  | 156 |
| 4.1 Introduction   | 157 |
| 4.2 Method   | 158 |
| 4.3 Results and Discussion   | 160 |
| 4.4 Implications   | 162 |
| 4.5 Conclusions and recommendations  | 164 |
| Acknowledgments  | 165 |
| References   | 165 |
| Figures  | 173 |
| <b>Chapter 5: Conclusions and future directions</b>  | 175 |
| References   | 181 |
| <b>Appendix: List of authored and coauthored publications</b>  | 184 |



## List of Tables and Figures

|   |    |
|---|----|
| Table 2.1: Initial conditions and results for isoprene-NO <sub>3</sub> aerosol yield experiments  | 72 |
| Table 2.2: Isoprene-NO <sub>3</sub> SOA products identified with UPLC/(-)ESI-TOFMS  | 73 |
| Table 2.3: Peroxide content of SOA formed by isoprene-NO <sub>3</sub> reactions   | 78 |
| Table 2.4: Global estimation of isoprene burdens and sinks using GEOS-Chem  | 79 |
| Figure 2.1: Time profiles of aerosol volume and inorganic nitrate measured by PILS/IC, and nitrate signals from Q-AMS in a blank experiment (~1 ppm N <sub>2</sub> O <sub>5</sub> , ammonium sulfate seed, no isoprene) | 80 |
| Figure 2.2: Isoprene depletion and SOA formation for typical experiment   | 81 |
| Figure 2.3: SOA yield data and yield curve for isoprene-NO <sub>3</sub> reaction.   | 82 |
| Figure 2.4: Time-dependent growth curves for the slow N <sub>2</sub> O <sub>5</sub> injection experiment and slow isoprene injection experiment   | 83 |
| Figure 2.5: Time profiles of the major gas-phase products ( <i>m/z</i> 230, 232, and 248) and the corresponding aerosol growth from the excess isoprene experiment  | 84 |
| Figure 2.6: Time evolution of various gas-phase products in the staggered N <sub>2</sub> O <sub>5</sub> injection experiment  | 85 |
| Figure 2.7: AMS spectrum for SOA formed in typical yield experiments  | 86 |
| Figure 2.8: AMS spectra signal from the slow N <sub>2</sub> O <sub>5</sub> injection experiment versus a typical yield experiment   | 87 |

|  |    |
|--|----|
| Figure 2.9: AMS spectra signal from the slow isoprene injection experiment versus a typical yield experiment   | 88 |
| Figure 2.10: UPLC/(-)ESI-TOFMS base peak ion chromatograms (BPCs) for isoprene-NO <sub>3</sub> oxidation experiments   | 89 |
| Figure 2.11: Proposed mechanisms for the formation of various gas-phase intermediate product ions observed by CIMS   | 90 |
| Figure 2.12: Time profiles of the major gas-phase products ( <i>m/z</i> 230, 232, and 248) and the corresponding aerosol growth from the slow N <sub>2</sub> O <sub>5</sub> injection experiment | 91 |
| Figure 2.13: Time profiles of the major gas-phase products ( <i>m/z</i> 230, 232, and 248) and the corresponding aerosol growth from the slow isoprene injection experiment                      | 92 |
| Figure 2.14: Proposed mechanism for SOA formation from the formation and decay of the C <sub>5</sub> -hydroxynitrate gas-phase product formed from the isoprene + NO <sub>3</sub> reaction       | 93 |
| Figure 2.15: Proposed mechanism for SOA formation from the formation and decay of the CIMS <i>m/z</i> 377 gas-phase product formed from the isoprene + NO <sub>3</sub> reaction                  | 94 |
| Figure 2.16: Proposed mechanism for SOA formation from the formation and decay of the CIMS <i>m/z</i> 393 gas-phase product formed from the isoprene + NO <sub>3</sub> reaction                  | 95 |

|   |     |
|---|-----|
| Figure 2.17: Proposed mechanism for SOA formation from the formation and decay of the C <sub>5</sub> -nitrooxycarbonyl, C <sub>5</sub> -hydroxycarbonyl, and C <sub>5</sub> dinitrate first-generation products formed from the isoprene + NO <sub>3</sub> reaction | 97  |
| Table 3.1: Gas-phase products of isoprene-NO <sub>3</sub> reaction detected by GC-FID and CIMS  | 148 |
| Table 3.2: Box model parameters for assessment of possible OH radical sources in isoprene-NO <sub>3</sub> system  | 149 |
| Figure 3.1: Generalized reaction mechanism for isoprene-NO <sub>3</sub> system.   | 150 |
| Figure 3.2: Formation of compounds resulting from isomerization of alkoxy radicals and seen by CIMS instrument at m/z 216, 246, 248, and 264  | 151 |
| Figure 3.3: Formation mechanism of methyl vinyl ketone, methacrolein, 3-methylfuran, and hydroxycarbonyl, leading to release of NO <sub>2</sub>   | 152 |
| Figure 3.4: Box model simulations for OH production in isoprene-NO <sub>3</sub> system  | 153 |
| Figure 3.5: Proposed formation mechanisms of products detected by CIMS at m/z 316, 330, 332, and 348  | 154 |
| Figure 3.6: Formation mechanism of dinitrooxyepoxide and hydroxyl radical from oxidation of nitrooxyhydroperoxide   | 155 |
| Figure 4.1: Mean elevation profiles of aerosol collision rates with OH, O <sub>3</sub> , H <sub>2</sub> O <sub>2</sub> during INTEX-NA campaign   | 173 |

Figure 4.2: Modeled vs. measured elevation profiles for acetaldehyde and peroxyacetic acid during INTEX-NA campaign