CAVITY RINGDOWN SPECTROSCOPY STUDIES OF ATMOSPHERIC REACTIONS: PEROXYNITROUS ACID FORMATION AND ALKOXY RADICAL ISOMERIZATION

Thesis by

Andrew Keeler Mollner

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

2007

(Defended May 18, 2007)

Acknowledgements

My graduate career has been a wonderfully rewarding experience. Caltech as an institution is ideal for graduate work, with minimal bureaucracy, skilled and caring support staff, and brilliant faculty, graduate students, and undergraduates. I have been particularly blessed to be supported by an amazing group of mentors, colleagues, friends and family.

First and foremost I would like to thank my advisors Drs. Mitchio Okumura and Stan Sander. Our weekly meetings have been a wonderful opportunity for me to tap into their wealth of knowledge and learn strategies for attacking scientific problems. As scientific advisors, they managed to provide me with both the freedom to develop my skills as an independent researcher and the guidance and support I needed to be productive. In addition to being wonderful teachers and mentors, Mitchio and Stan are also kind and generous people. I have never doubted that they sincerely care about me, both as a scientist and a person, and I will always consider them both mentors and friends.

I also owe a great deal of thanks to the many people I have had the pleasure of working with in 17 Noyes who contributed immensely to the work described in this thesis. Many of my lab skills were passed down from Drs. Sergey Nizkorodov and Brian Bean, who showed me the ropes my first year in lab. They shared with me not only their scientific knowledge, but also their enthusiasm for the research. They were both wonderful teachers and treated me from day one as colleague rather than a subordinate. In particular, Brian spent many patient days forcing me to align lasers, ringdown cavities,

and detectors so that I could learn these skills, when I'm sure he could have done it all himself in a fraction of the time. Later in my career, I was fortunate to have three other experienced researchers, Drs. Leah-Nani Alconcel, Lin Feng, and Eva Garland, as co-workers in lab. Each of them shared with me knowledge gained from their graduate experiences and helped immensely in progressing my research.

My graduate career was also greatly enriched by several opportunities I have had to act as a mentor. I have had three undergraduates work with me as part of the Summer Undergraduate Fellowship Program, Gautham Nair, Terry Yen, and Alex Padilla as well as one high school student Da Lin. All of them were enthusiastic, hard working, and wonderful people to spend summers with. I also must express my gratitude to my latest apprentice, Matthew Sprague, who has taken over for me as the graduate student in 17 Noyes. He has been a joy to work with and his efforts the past year have contributed greatly to this thesis. I hope that I have been able to give him the same quality tutelage I received from my mentors.

I have also benefited greatly from the support of the Okumura group as a whole. The group office is a friendly, happy, and collaborative place to work where you can always find advice and support when problems arise. I like to think the incoming class of 2001 (myself, Julie Fry and David Robichaud) is partly responsible for fostering this wonderful group dynamic. I must give special thanks to the group Labview guru David Robichaud. David not only wrote the program which collected nearly all the data contained in this thesis, but had the skill and patience to walk me through understanding how it works and how to modify it. I would also like to thank current members of the

group David Robichaud, Aaron Noell, Laurence Yeung, Kana Takematsu, Matthew Sprage, and Kathleen Spencer, for their feedback on my propositions and this thesis.

I would also like to thank several staff and faculty for their contributions to my work. Dave Natzic of the Sander group was tremendously helpful in getting my lab running again several times when things went awry. Rick Gerhart in the Caltech glass shop and Mike Roy in the Caltech machine shop have also been instrumental, not only through their wonderful craftsmanship but also through their knowledge and advice. Thanks also to my committee members for their feedback on my Candidacy, Propositions, and Thesis: Pat Collier, Mitchio Okumura, Stan Sander, Nate Lewis, and Paul Wennberg.

Finally, I firmly believe that a happy graduate student is a productive graduate student and I owe thanks to many people outside of my research for helping keep me happy. Bill Bing and the Caltech-Occidental Concert Band provided me with a wonderful outlet for my inner musician. My various intramural sports teams, in particular Team Justice, Imperial Palace, and FBOD were a great group of friends and ensured I exercised regularly. It has also been wonderful to be near my family. I am fortunate to have had them provide me with unconditional love (as well as occasional food and laundry) during my graduate career.

Finally I would like to try and express my gratitude to my wife Rebecca. She has been a constant source of love, joy, and inspiration. No matter how well or how poorly things went in lab, I could always count on being happy when I went home and I cannot thank Rebecca enough for that.

Abstract

This thesis describes laboratory experiments investigating atmospheric reactions using cavity ringdown spectroscopy (CRDS). The reactions studied were the formation of peroxynitrous acid (HOONO) in the termolecular association reaction OH + NO_2 (R1) and the isomerization of alkoxy radicals. Experiments were conducted in a gas flow cell combining UV photolysis to initiate reactions with infrared CRDS for the detection of products.

Formation of the weakly bound HOONO in the atmosphere reduces the yield of nitric acid ($HONO_2$) from R1 and lowers the efficiency of R1 as a sink for radicals. The *cis-cis* conformer of HOONO was detected through its fundamental ν_1(OH-stretch) spectrum centered at 3306 cm^{-1}. The integrated absorbance of the ν_1 bands for HOONO and $HONO_2$ were measured with CRDS and used to calculate the branching ratio (BR = k_{HOONO} / k_{HONO2}) of R1. Initial experiments using a microwave discharge to initiate R1 measured BR at 298 K and 14 torr, but were limited to low pressures by the discharge. BR was then reinvestigated using pulsed laser photolysis to initiate R1. BR was measured over the range 20–760 torr at 298 K.

In support of these branching ratio measurements, a detailed study of the spectroscopy of $HONO_2$ was conducted. CRDS experiments with moderate resolution (1 cm^{-1}) are known to give incorrect absorbances and line shaes when measuring spectral features with much narrower linewidths. However, the magnitude of these CRDS errors when probing a highly congested spectrum such as that of $HONO_2$ was unknown. We

observed reductions in the $HONO_2$ integrated intensity up to 60% and quantified these errors as a function of concentration and pressure.

Alkoxy radicals (RO) are an important class of intermediates in the oxidation of hydrocarbons, and they react via several mechanisms. For longer chain RO isomerization (forming HOR) becomes a major pathway, but isomerization rates have never been directly measured. Continuing work described in Eva Garland's thesis, we measured the infrared spectrum of alkoxy radical isomerization products (HOR and $HORO_2$) formed within 100 μs. We then used this spectrum to measure the relative rate of isomerization to reaction with oxygen for n-butoxy and 2-pentoxy radicals.

TABLE OF CONTENTS

List of Figures

List of Tables