PHOTOCHEMISTRY OF PYRUVIC ACID IN WATER AND ICE

Thesis by

Marcelo Ioel Guzmán

In Partial Fulfillment of the Requirements

for the degree of

Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

2007

(Defended October 12, 2006)

ACKNOWLEDGEMENTS

I am grateful to my advisor, Michael R. Hoffmann, for allowing me the opportunity to work through these years at Caltech; for giving me the freedom, since my first day, to be creative and productive in science; for his guidance, encouragement, and understanding. Special thanks to Agustin J. Colussi, for all his scientific help and constant support, for taking my research very seriously, and for sharing his experience and critical view of science as well as for his guidance in this process. His enthusiastic advice was invaluable in my research. They have both created an excellent environment in the Keck Lab for learning and exploring new questions in the field of ice chemistry (among many other fields).

Furthermore, I am grateful for the feedback the following professors provided me: Paul Wennberg, Janet Hering, John Seinfeld, Richard Flagan, and Yuk Yung. I am very thankful to anonymous reviewers who have contributed substantially by through critical comments to the improvement of the chapters that have been already published in peer review journals.

Thanks to Nathan Dalleska, Sonjong Hwang, Angel Di Bilio, and Peter Babilo for helping me with many technical aspects of my research.

I am also greatly thankful to my current and former lab and office mates Chris Boxe, Chad Vecitis, Megan Ferguson, Bill Balcerski, Marta Mrowetz, Tim Lesko, Jina Choi, Jie Cheng, Su Young Ryu, and Fok-Yan Leung, for all their help, knowledge, support, and friendship all these years.

In addition, I would also like to acknowledge Linda Scott, Cecilia Gamboa, Jose Diaz, Elena Escot, and Fran Matzen for all of their help and patience with me.

I would also like to express my gratitude to Tonci Crmaric, Shahin Rhaman, Michelle Friedman, Sally Nga Lee Ng, Dmitry Pavlov, Alan Miller, and Alan Kwan for their friendship and interesting discussions.

I appreciate the advice of Maria Eugenia Hernandez and my undergraduate professors Juan Carlos Diaz Ricci and Bernardo Guzman, who had an enormous influence on my decision to attend to Caltech. Special thanks to Silvia Centeno, for her encouragement in the beginning.

All my love and thanks to my parents, Marta and Bernardo, and to all the people who encouraged me to aim high and reach my goals.

The research presented in this dissertation was funded in part through a Vito Vanoni Fellowship from funds provided by the Davidow Environmental Initiative and from a grant from the National Science Foundation.

M. I. G., Pasadena, August 24, 2006

ABSTRACT

The 321 nm band photodecarboxylation of aqueous pyruvic acid, PA, solutions was studied over the range $5 \leq [PA] \leq 100$ mM. Immediate and delayed CO_2 production stages were detected using TEMPO as a scavenger. During the irradiation of frozen aqueous solutions of PA, CO_2 evolution occurs; however, additional CO_2 is released in the absence of light. The release rate under dark conditions was found to be first order in $[CO_2]$ with an activation energy $E_a \sim 22$ kJ mol^{-1} at $T < 268$ K. Photodecarboxylation rates of anoxic aqueous PA solutions decreased two-fold in the frozen state at 253 K relative to the liquid state at 293 K. In contrast, there was no post-illumination emission of CO_2 during the photodecomposition of benzoylformic acid in frozen solutions.

Magic angle spinning ^{1}H-NMR measurements were made to determine the hydration state of aqueous PA between the carbonyl and its hydrated gem-diol counterpart, PAH. In the frozen state, the fraction of the photoactive carbonyl-form of PA, approaches ~ 20% at temperatures below 263 K, regardless of the initial PA concentration over the range $0.1 \text{ M} \leq [PA] \leq 4.6$ M. Calculations show that ~ 4 water molecules are involved in the hydration of PA in ice at 243 K. Pyruvic acid is cooperatively hydrated while dissolved, or partitioned into viscous aqueous microfluids often called quasi liquid layers (QLL) down to the glass transition.

Electron magnetic resonance measurements of frozen aqueous solutions of PA that were irradiated at $\lambda = 313$ nm and at $T = 77$ K were determined to be distant triplet radical pairs separated by approximately 0.9 nm. These triplet pairs are formed by photoinduced electron transfer between a triplet excited state of PA and corresponding ground state of PA

to produce $^{3}[PA^{+\cdot}\ PA^{-\cdot}]$. The subsequent deprotonation of $PA^{+\cdot}$ into an acylcarbonyloxyl radical which undergoes an ultrafast decarboxylation, accounts for the post-illuminated CO_2. Liquid chromatography with UV and ESI-MS detection combined with ^{13}C-isotope labeling techniques were used to identify products. The protonated radical anion $PA^{-\cdot}$ (i.e., a ketyl-radical) self-reacts to form 2,3-dimethyltartaric acid. Another pathway involving reaction of the ketyl radical with ground-state PA forms an unstable β-keto dicarboxylic acid, which undergoes CO_2 elimination to produce 2-(3-oxobutan-2-yloxy)-2-hydroxypropanoic acid.

In conclusion, the possibility of photolysis in ice core records due to penetrating Cerenkov radiation derived from cosmic rays is explored. Potential impacts of the photolysis of organic matter trapped in ice with the subsequent release of CO and CO_2 over the last two millennia is analyzed.

TABLE OF CONTENTS

LIST OF FIGURES, SCHEMES, AND TABLES