

# **Chemical Effects of Acoustic Cavitation**

Thesis by

Timothy Michael Lesko

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

2004

(Defended April 21, 2004)

© 2004

Timothy Michael Lesko

All Rights Reserved

**To my family**

## Acknowledgements

First and foremost, I would like to thank my advisor, Michael Hoffmann, for his acceptance of me into his group and his patience in allowing me to pursue the projects that interested me. I am grateful for the support and incredible understanding he showed throughout my graduate studies. Also, I wish to thank my examining committee: Profs. Vincent McKoy, Jacqueline Barton, and Nathan Lewis.

I am also grateful to my colleagues in the Keck Laboratories, especially to Dr. A.J. Colussi, who shared with me so much knowledge and passion about chemistry, politics, and fine arts. A.J. helped me prioritize my goals and taught me when to put down the wrench and pick up the pen. Hui-Ming Hung and Hugo Destailats gave me a warm introduction to the lab and to sonochemistry. Yael Dubowski gladly taught me Hebrew even after I stole her lab bench. I cannot forget the other members of the Hoffmann, Hering, and Leadbetter groups who have helped along the way including: Bill Balcerski, Chris Boxe, Weng-Ki Ching, Suvasis Dixit, Suvi Flagan, Daniel Giammar, Marcelo Guzman, Jong-In Han, Janet Hering, Jean Huang, Alan Kwan, Jared Leadbetter, Giehyeon Lee, Fok-Yan Leung, John Moss, Tina Salmassi, Jennie Stephens, Steve Szczepankiewicz, Chad Vecitis, Yajuan Wang, Nermin Vural, and Wanwan Yang.

The undergraduates who worked with me over several summers are also very much appreciated. Thomas Alderson II assisted with many of the experiments run in the “big reactor” in Chapter 3. Tommy Trieu gladly spent a portion of his SURF project helping me tear apart and repair this same reactor after we managed to push it to its limits the following summer. His upbeat attitude and willingness to shift projects midstream

made many of the experiments in Chapter 4 possible. Russeen 'Paul' Wali did a great job assisting me with the oxalate experiments and always kept me laughing.

There are so many people at Caltech who have helped me and who have been fantastic friends over the years. Kate Campbell and Megan Alameda Knight-Pratt-Ferguson taught me that in addition to accelerating chemical reactions, sound waves can also make my feet dance. When not helping me surmount problems with my analytical instrumentation, I could always bend the ears of Jeff Noelte, Nathan Dalleska, or Bob Becker to discuss cars or woodworking. Bob, we all miss you. Keliann and M.J. LeConte were always ready to listen, even as I viciously tormented their bird. Lisa Cowan always had time for a hug or a recitation of the "pirate's alphabet." Linda Scott, Fran Matzen, and Irene Loera were my Caltech "moms," who made sure I ate and let me complain on their shoulders. Mike Vondrus was always willing to share with me his mechanical genius, not to mention his culinary talents. Belinda Campbell always had a warm smile for me and Elena Escot was a wonderful maestra. Special thanks must be extended to Dian Buchness and Jonie Watanabe for keeping me on track.

I am also thankful to Jack McQueen and Warren Weber, who had faith in me to care for their Mill. My own "This Old House" - Bees and Coyotes and Skunks, Oh My! My wonderful neighbors, the Quinn's and the Knox's, always provided me with new and interesting challenges that kept my tools and mind sharp and my stomach full.

Finally, I cannot thank my parents and my sister, Becca, enough for all of their support over the years. Your encouragement and love have helped me through some difficult times and have helped make me the person I am today. I owe the three of you so much - work on your entertainment centers and desks will soon be under way!

## Abstract

A novel high-frequency, high-power, pilot-plant scale sonochemical reactor was developed and used to study the degradation of dichloromethane, trichloroethylene, phenol, and methyl orange in aqueous solutions. The degradation rates of trichloroethylene, dichloromethane, and phenol were found to exceed those of similar frequency, small-scale bench reactors by factors ranging from 2.5 to 7. The degradation of these compounds was found to be inversely related to their initial concentrations. Experiments with 10  $\mu\text{M}$  methyl orange in the large reactor operating at different total volumes exhibited a linear dependence between the observed sonolytic rate constants and the applied power density. Likewise, steady-state  $\cdot\text{OH}$  (aq) in each reactor were calculated and shown to correlate with the applied power density in the vessel. Comparisons of the power density utilization between sonochemical methods and photocatalytic techniques applied to the same chemical systems show an improvement of up to two orders of magnitude of efficiency when ultrasonic irradiation is employed.

The sonochemical decomposition of phenol was further studied in a bench-scale ultrasound reactor combination with ozonolysis. The addition of ozone during sonication did not affect the first-order degradation rate constants of phenol compared to the linear combination of separate sonication and ozonation experiments. However, enhancement of the degradation rates of the total organic carbon (TOC) by 43% was observed for sonolytic ozonation compared to the separate sonication and ozonolysis experiments. Complete mineralization of phenol to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  was only achieved using the simultaneous application of these two systems. A comparison of phenol's TOC degradation profiles using various combinations of these two techniques reveals that the

combined system is capable of degrading unsaturated organic daughter products (*e.g.*, oxalic acid) which are not susceptible to direct reactions with molecular ozone. The synergistic action of  $O_3$  (aq) and ultrasound enhanced oxalate degradation rates 16-fold compared to the simple linear addition of the two independent systems. Several degradation pathways, including a new chemical mechanism, are considered which may account for the rate enhancements observed when ultrasonic irradiation is applied concurrently with ozonolysis.

In addition, the decomposition of aqueous ozone in the presence of hydrogen peroxide was investigated.  $H_2O_2$  enhances the reactivity of  $O_3$  (aq) by reactions that remain obscure. Several free-radical degradation mechanisms for  $O_3$  decomposition correctly predict the ozone-decay kinetics in pure water but vastly overestimate reaction rates in the presence of  $H_2O_2$ . Results from solvent deuteration experiments in neat water are compatible with a chain-process driven by electron transfer and/or O-transfer processes. However, the large kinetic isotope effect (KIE) found in the  $O_3/H_2O_2$  system provides compelling evidence for an elementary reaction ( $O_3 + HO_2^-$ ) involving H– $O_2^-$  bond cleavage and does not support appreciable radical production from the  $O_3 + HO_2^-$  reaction. The magnitude of the observed KIE is consistent with a hydride transfer process yielding a closed-shell trioxide  $HO_3^-$ , the conjugate anion of  $H_2O_3$ .

**Table of Contents**

Acknowledgements		iv
Abstract		vi
Chapter 1	Overview	1
Chapter 2	Background	9
Chapter 3	Scale-Up of Sonochemical Reactors for Water Treatment	37
Chapter 4	Sonochemical Decomposition of Phenol: Evidence for a Synergistic Effect of Ozone and Ultrasound for the Elimination of Total Organic Carbon	79
Chapter 5	Hydrogen Isotope Effects and Mechanism of Aqueous Ozone and Peroxone Decompositions	119
Chapter 6	Decomposition of Oxalate in Dilute Aqueous Solutions: Evidence for the Strong Synergism of Ozonolysis Combined with Ultrasonic Irradiation	143
Chapter 7	Conclusions	187