Chapter 1

Overview

The chemical effects resulting from the irradiation of aqueous solutions with ultrasound were first reported in 1927.[1,2] Since then, a wide variety of sonochemical reactions pertaining to inorganic[3-5] and organic synthesis,[6-9] polymerization,[10-12] and electrochemistry[13-15] have been developed. While ultrasound was found to be effective at promoting these chemical reactions, restricted reactor volumes, difficulties controlling the extent of the synthesis, and relatively high operating costs have hindered the scaling-up of many of these systems.[16-18] However, one application where large-scale sonochemical processing may be feasible is for drinking water purification and wastewater remediation. Major concerns about the toxic and mutagenic byproducts of chlorination, and the implementation of more stringent regulations,[19-21] have renewed interest in this public sector for alternative treatment processes. One such treatment may be ultrasonic irradiation, which has been shown to be effective for the treatment of a wide variety of aqueous organic pollutants.[22-46] The use of ultrasound is particularly attractive because it yields hydroxyl radicals, ·OH, *in situ*. This highly and universally reactive species is effective for degrading organic pollutants which are found to be recalcitrant toward conventional chemical oxidants.

In an effort to increase the efficiency and decrease the overall cost of sonochemical treatment systems, several investigation have examined the combination of ultrasonic irradiation with ozonolysis.[47-51] In most cases, these studies found that when these systems are used simultaneously, the degradation of many solutes becomes faster than predicted by the addition of the independent effects. Rate enhancements have been attributed to the increased production of free radical species in solution; however, the exact mechanism of this synergism is not fully understood.

The primary goals of our research were to elucidate the mechanism underlying the observed synergism and to optimize the processing of aqueous organic pollutants under simultaneous ultrasonic irradiation and ozonation. As a result, we have gained new insights into the chemical mechanisms of free-radical production in these oxidation systems. This knowledge will be useful in the design of improved sonochemical wastewater treatment protocols.

The development and evaluation of a new pilot-scale ultrasound reactor is the subject of Chapter 3. This state-of-the-science system represents the first large-scale ($V \geq 7.25$ L), high-frequency, high-power reactor of its kind. The sonochemical efficiency of this system was investigated using four organic compounds, dichloromethane (DCM), trichloroethylene (TCE), phenol, and methyl orange (MO). The degradation kinetics of these solutes were investigated as a function of reactor flow rate, initial solute concentration, treatment volume, and power density.

The decomposition of phenol and its eventual oxidation to CO_2 and H_2O are discussed in Chapter 4. These reactions were investigated with ultrasonic irradiation and ozonolysis in a lab-scale ultrasound reactor. Optimal reaction conditions were explored with respect to ozone dose, initial solute concentrations, background gas composition, ultrasonic frequency, and power density. The concurrent application of the two techniques was found to significantly improve the mineralization of phenol. A mechanism is proposed that accounts for such enhancement.

The principal objective in Chapter 5 is to investigate the chemistry that results from the addition of hydrogen peroxide to aqueous ozone solutions. Ozone decay kinetics were measured as a function of H_2O_2 concentrations at low pH in H_2O and D_2O

solutions. Chemical models based on elementary reactions were compared to experimental results to elucidate a new mechanism of peroxone action.

Chapter 6 deals with the strong synergism of ultrasonic irradiation combined with ozonolysis for the decomposition of oxalic acid, a particularly refractory pollutant. In addition to optimizing solute degradation rates with respect to ozone concentration and ultrasound power density, the effects of pre-sonication and hydrogen peroxide production were investigated. Various mechanisms were explored to account for the enhanced production of free-radical intermediates in the combined systems. These mechanisms were evaluated by investigating the sonolytic decomposition of ozone in the presence and absence of oxalic acid.

References

(1) Richards, W.; Loomis, A. *J. Am. Chem. Soc.* **1927**, *49*, 3086.

(2) Wood, R.; Loomis, A. *Phil. Mag.* **1927**, *4*, 414.

(3) Lindley, J. Sonochemical Aspects of Inorganic and Organometallic Chemistry Including Catalysis. In *Chemistry with Ultrasound*; Mason, T., Ed.; Elsevier Applied Science: New York, 1990; pp 27.

(4) Suslick, K.; Hyeon, T.; Fang, M.; Ries, J.; Cichowlas, A. *Mater. Sci. Forum* **1996**, *225*, 903.

(5) Suslick, K.; Price, G. *Annu. Rev. of Mat. Sci.* **1999**, *29*, 295.

(6) Davidson, R. Ultrasonically Assisted Organic Synthesis. In *Chemistry with Ultrasound*; Mason, T., Ed.; Elsevier Applied Science: New York, 1990; pp 65.

(7) Low, C. Ultrasound in Synthesis: Sonochemistry as a Tool for Organic Chemistry. In *Current Trends in Sonochemistry*; Price, G., Ed.; The Royal Society of Chemistry: Cambridge, 1992; pp 59.

(8) Mason, T. *Chem. Soc. Rev.* **1997**, *26*, 443.

(9) Cains, P.; Martin, P.; Price, C. *Org. Process Res. Dev.* **1998**, *2*, 34.

(10) Lorimer, J. Polymers. In *Chemistry with Ultrasound*; Mason, T., Ed.; Elsevier Applied Science: New York, 1990; pp 115.

(11) Price, G. Ultrasonically Assisted Polymer Synthesis. In *Current Trends in Sonochemistry*; Price, G., Ed.; The Royal Society of Chemistry: Cambridge, 1992; pp 87.

(12) Price, G. *Ultrasonics Sonochemistry* **2003**, *10*, 277.

(13) Compton, R.; Eklund, J.; Marken, F. *Electroanalysis* **1997**, *9*, 509.

(14) Lorimer, P.; Mason, T. *Electrochemistry* **1999**, *67*, 924.

(15) Walton, D. *ARKIVOK Journal* **2002**, *3*, 198.

(16) Mason, T. *Ultrasonics Sonochemistry* **2000**, *7*, 145.

(17) Mason, T. *Philos. Trans. R. Soc. London, Ser. A* **1999**, *357*, 355.

(18) Mason, T. Ultrasound in Industrial Processes: The Problems of Scale-Up. In *Current Trends in Sonochemistry*; Price, G., Ed.; The Royal Society of Chemistry: Cambridge, 1992; pp 158.

(19) Hwang, B.; Jaakkola, J. *Arch. Environ. Health* **2003**, *58*, 83.

(20) Bove, F.; Shim, Y.; Zeitz, P. *Environ. Health Persp.* **2002**, *110*, 61.

(21) Faust, S.; Aly, O. *Chemistry of Water Treatment*, Second Edition ed.; Ann Arbor Press: Chelsea, Michigan, 1998.

(22) Phull, S.; Mason, T.; Lorimer, J.; Newman, A.; Pollet, B. *Ultrasonics Sonochemistry* **1997**, *4*, 157.

(23) Gonze, E.; Fourel, L.; Gonthier, Y.; Boldo, P.; Bernis, A. *Chem. Eng. J.* **1999**, *73*, 93.

(24) Kotronarou, A.; Mills, G.; Hoffmann, M. *J. Phys. Chem.* **1991**, *95*, 3630.

(25) Naffrechoux, E.; Chanoux, S.; Petrier, C.; Suptil, J. *Ultrasonics Sonochemistry* **2000**, *7*, 255.

(26) Beckett, M.; Hua, I. *Environ. Sci. Technol.* **2000**, *34*, 3944.

(27) Beckett, M.; Hua, I. *J. Phys. Chem. A* **2001**, *105*, 3796.

(28) Destaillats, H.; Lesko, T.; Knowlton, M.; Wallace H; Hoffmann, M. *Ind. Eng. Chem. Res.* **2001**, *40*, 3855.

(29) Joseph, J.; Destaillats, H.; Hung, H.; Hoffmann, M. *J. Phys. Chem. A* **2000**, *104*, 301.

(30) Mason, T.; Lorimer, J. *Applied Sonochemistry: The Uses of Power Ultrasound in Chemistry and Processing*; Wiley-VCH: Darmstadt, Germany, 2002.

(31) Peller, J.; Wiest, O.; Kamat, P. *J. Phys. Chem. A* **2001**, *105*, 3176.

(32) Petrier, C.; Francony, A. *Ultrasonics Sonochemistry* **1997**, *4*, 295.

(33) Hua, I.; Hoffmann, M. *Environ. Sci. Technol.* **1997**, *31*, 2237.

(34) Kotronarou, A.; Mills, G.; Hoffmann, M. *Environ. Sci. Technol.* **1992**, *26*, 2420.

(35) Berlan, J.; Trabelsi, F.; Delmas, H.; Wilhelm, A.; Petrignani, J. *Ultrasonics Sonochemistry I* **1994**, 1994.

(36) Colussi, A.; Hung, H.; Hoffmann, M. *J. Phys. Chem. A* **1999**, *103*, 2696.

(37) Drijvers, D.; Van Langenhove, H.; Beckers, M. *Water Res.* **1999**, *33*, 1187.

(38) Entezari, M.; Petrier, C.; Devidal, P. *Ultrasonics Sonochemistry* **2003**, *10*, 103.

(39) Jiang, Y.; Petrier, C.; Waite, T. *Ultrasonics Sonochemistry* **2002**, *9*, 163.

(40) Lin, J.; Ma, Y. *J. Haz. Mat. B.* **1999**, *66*, 291.

(41) Mark, G.; Schuchmann, H.; von Stonntag, C. *J. Am. Chem. Soc.* **2000**, *122*, 3781.

(42) Okouchi, S.; Nojima, O.; Arai, T. *Water Sci. Technol.* **1992**, *26*, 2053.

(43) Petrier, C. *J. Phys. Chem.* **1994**, *98*, 10514.

(44) Rong, L.; Yasuda, K.; Bando, Y.; Nakamura, M. *Jpn. J. Appl. Phys.* **2002**, *41*, 3272.

(45) Seymour, J.; Gupta, R. *Ind. Eng. Chem. Res.* **1997**, *36*, 3453.

(46) Takizawa, Y.; Akama, M.; Yoshihara, N.; Nojima, O.; Arai, K.; Okouchi, S. *Ultrasonics Sonochemistry* **1996**, *3*, S201.

(47) Weavers, L.; Malmstadt, N.; Hoffmann, M. *Environ. Sci. Technol.* **2000**, *34*, 1280.

(48) Olson, T.; Barbier, P. *Water Res.* **1994**, *28*, 1383.

(49) Destaillats, H.; Colussi, A.; Joseph, J.; Hoffmann, M. *J. Phys. Chem.* **2000**, *104*, 8930.

(50) Barbier, P.; Petrier, C. *J Adv. Oxid. Technol.* **1996**, *1*, 154.

(51) Kang, J.; Hung, H.; Lin, A.; Hoffmann, M. *Environ. Sci. Technol.* **1999**, *33*, 3199.