

# **Chemical Effects of Acoustic Cavitation**

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**To my family**

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## 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