Chapter 7

Conclusions

The use of ultrasonic irradiation, alone or in combination with ozonation, has been shown to enhance a variety of different chemical reactions in aqueous solution. In Chapter 3, we demonstrated the potential of a novel high-frequency, high-power, pilot-scale sonochemical reactor for the processing of deleterious and refractory chemical compounds. Degradation rates of trichloroethylene, dichloromethane, and phenol in the scaled-up reactor were found to be 2.5 - 7 times larger than the observed rates in bench-scale experiments performed at ~ 1/10 of the volume volume. The degradation rates of 10 μM methyl orange in the pilot-scale reactor increased linearly with applied power density (PD), in the range $67 < PD (W/L) < 414$. Sonochemical processesing in this reactor exhibit energy efficiencies that are up to two orders of magnitude higher than the corresponding efficiencies for treating similar media with TiO_2 photocatalysis technology.

The interaction of ozone and ultrasound for the degradation of phenol was investigated in a bench-scale sonochemical reactor. In this case, the combination of these agents induced linearly additive effects. In contrast, the reduction of the total organic carbon (TOC) in these systems exhibited significant synergism. TOC loss rates were found to be dependent on both the aqueous O_3 concentration and ultrasonic power density. Under optimal conditions, the simultaneous application of ultrasonic irradiation and ozone enhanced TOC decomposition rates by 43% over the sum of the rates obtained by separate treatments. The evolution of intermediate species detected during the degradation of phenol indicates that while the primary products are efficiently oxidized by simple ozonolysis, subsequently generated species require simultaneous ultrasonic treatment.

During the course of these experiments, evidence was obtained suggesting that H_2O_2, a sonochemical product of water decomposition, enhanced O_3 reactivity toward oxalate, a highly recalcitrant by-product. In order to elucidate the mechanism of apparent enhancement, the decomposition of aqueous ozone in the absence and presence of hydrogen peroxide in H_2O and D_2O as solvents was investigated in detail. We found that the reaction between O_3 and HO_2^- does not produce free-radicals, but proceeds via a hydride transfer into a closed-shell trioxide species, HO_3^-. We postulate that the enhanced reactivity of O_3/H_2O_2 mixtures is due to the participation of HO_3^-. Because H_2O_3/HO_3^- may be involved in various biological, atmospheric, and environmental oxidative processes, further research into the reactivity of this intermediate species is warranted.

The enhanced efficiency of the combined (ultrasound + ozone) treatement was demonstrated in the mineralization of oxalate ($HC_2O_4^-$). Oxalate degradation rates were found to be more than 16 times faster than the sum of independent effects. Model calculations and batch ozone decomposition experiments in the presence of $HC_2O_4^-$ suggest that ozone efficiently reacts with the carboxyl anion radical, $CO_2^-\cdot$ produced by OH-radical attack on $HC_2O_4^-$. We propose that this reaction propagates a free-radical chain mechanism which can sustain an elevated steady-state OH-radical concentrations. We believe that this mechanism is responsible for the rapid degradation of $HC_2O_4^-$, perhaps magnified by the additional production of OH-radicals that results from the sonochemical decomposition of O_3. Oxalate can be also oxidized by the H_2O_2/O_3 mixture. However, H_2O_2 addition to systems undergoing sonolytic ozonation did not appreciably affect degradation kinetics, indicating that the O_3/ultrasound/$HC_2O_4^-$ system is predominantly driven by free-radical chemistry.

In summary, we have (1) found a substantial synergism in the combination of ozonation and soniciation for the mineralization of oxalate, a relatively recalcitrant anionic species that constitutes the normal endpoint of conventional oxidation of dissolved organic matter; (2) provided compelling evidence in favor of a free-radical mechanism for this phenomenon; and (3) shown for the first time that the chemistry of O_3 and H_2O_2 in aqueous solution involves a novel reaction intermediate HO_3^-/H_2O_3.