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Cavitational Hydrothermal Oxidation: A New Remediation Process

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Research Objective

Our primary goal is to develop a quantitative understanding of cavitation phenomena in aqueous media and the development of applications of cavitation to remediation processes. Our efforts have focused on three separate areas: sonoluminescence as a probe of conditions created during cavitational collapse in aqueous media, the use of cavitation for remediation of contaminated water, and an addition of the use of ultrasound in the synthesis of novel heterogeneous catalysts for hydrodehalogenation of halocarbons under mild conditions.

Research Progress and Implications

This report summarizes work after one year of a three year project.

In order to gain further understanding of the conditions present during cavitation, we have continued our studies of sonoluminescence [1]. We have made recent breakthroughs in the use of emission spectroscopy for temperature and pressure measurement of cavitation events, which we expect to publish shortly. We have been able to measure *for the first time* the temperature of cavitation *in water* during multi-bubble cavitation in the presence of aromatic hydrocarbons [2]. The emission from excited states of C_2 in water gives temperatures that are consistent with adiabatic compressional heating, with maximum temperatures of 4300° K. Our prior measurements of cavitation temperatures in low vapor pressure nonaqueous media gave somewhat higher temperatures of 5000 K [1]. This work lays permanently to rest exotic mechanisms for cavitational chemistry, at least for cavitation fields.

In a new avenue of research, we have recently explored the generation of cavitation by hydrodynamic techniques and demonstrated for the first time that chemical reactions occur during turbulent flow of water and of water containing chlorocarbons [3]. This work received substantial publicity. While the chemical effects of *acoustic* cavitation (i.e., sonochemistry and sonoluminescence) have been extensively investigated during recent years, little is known about the chemical consequences of *hydrodynamic* cavitation created during turbulent flow of liquids. Hydrodynamic cavitation is observed when large pressure differentials are generated within a turbulent liquid flow and is accompanied by a number of physical effects, erosion being most notable from a technological viewpoint. It has the potential advantage of facile scale-up: there already exist commercial high pressure flow mixing units capable of generating hydrodynamic cavitation with flows of 50 gpm (Microfluidics, Inc., Newton, MA). However, prior reports of hydrodynamically induced chemistry or luminescence and direct comparisons to sonochemistry or sonoluminescence have been extremely limited. The oxidation of iodide to triiodide in aqueous solutions containing halocarbons (e.g., $CHCl_3$ or CCl_4) under hydrodynamic cavitation conditions was examined in order to determine the origin of this hydrodynamic chemical reaction. This reaction also serves as a model for remediation of halocarbon contaminated water using hydrodynamic cavitation, a previously unexplored approach to remediation. The effects of several experimental variables on the I_3^- production rate were investigated. Increasing the reaction temperature inhibits the I_3^- production due to increased vapor pressure, which leads to reduced efficacy during cavitational collapse; the rate decreases exponentially with vapor pressure. The production of I_3^- is sensitive to the nature of the dissolved gas and decreases exponentially with increasing gas thermal conductivity. Thus, the chemistry observed and its response to external parameters is remarkably similar to ultrasonically induced cavitation, albeit the sonochemical rates are significantly higher at least with our current experimental configurations.

Planned Activities

Our overall goal in this research is to develop our understanding of the reactions of organic compounds in the presence of high intensity ultrasound. To approach this goal, our planned activities will continue in three areas: 1) investigation of the local conditions formed during cavitation in water; 2) mechanistic examination of the effects of cavitation on aromatic hydrocarbons and halocarbons, and 3) determination of degradation yields as a function of experimental configurations for cavitation production with aromatics and halocarbons as toxic impurities in water. In all cases, we will continue our special emphasis on the mechanistic origins of sonochemistry, in relationship to its applications to environmental challenges. Information gained should lead to effective protocols and equipment for large scale treatment of contaminated water and soil.

We have also developed a new research area relevant to environmental remediation chemistry that derives from our recent discovery of the catalytic *hydrodehalogenation* of halocarbons. In work not funded by the DOE, we have been actively involved in the development of sonochemical preparations of active heterogeneous catalysts [4-6]. The localized hot-spot created during acoustic cavitation is sufficient to strip ligands completely from metal complexes. This process also produces enormous cooling rates ($>10^9$ K/s) and so allows the formation of colloidal, amorphous metal aggregates. We have very recently used ultrasound to produce nanostructured MoC_2 with very high surface areas and excellent catalytic activity [7]. Our most recent discovery is very relevant to our DOE project, however: this sonochemically prepared MoC_2 is an extremely effective and stable *hydrodehalogenation* catalyst. In gas flows with H_2, we can remove both Cl and F from essentially all halocarbons, replacing the halogen with hydrogen quantitatively and quickly without degradation of the MoC_2 catalyst (in spite of the release of HCl or HF which rapidly destroy most other catalysts), under mild conditions (<300° C). We have examined quantitatively the catalytic properties of supported catalysts produced sonochemically from using gas/solid microreactor kinetics monitored by GC/MS. We expect to publish this work in the near future.

Other Access To Information

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