Chemistry Induced by Hydrodynamic Cavitation

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Cavitation (the formation, growth, and implosive collapse of gas or vapor-filled bubbles in liquids) can have substantial chemical and physical effects. While the chemical effects of *acoustic* cavitation (i.e., sonochemistry and sonoluminescence) have been extensively investigated during recent years,[1–5] 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 moving liquid and is accompanied by a number of physical effects, erosion being most notable from a technological viewpoint.[6,7] In contrast, reports of hydrodynamically induced chemistry or luminescence and direct comparisons to sonochemistry or sonoluminescence have been extremely limited.[8,9]

In aqueous liquids, acoustic cavitation leads to the formation of reactive species such as OH•, H•, and H_2O_2. These short-lived species are capable of effecting secondary oxidation and reduction reactions. For example, iodide can be sonochemically oxidized to triiodide by OH• radicals or H_2O_2 produced during cavitation. From aqueous solutions containing chlorocarbons, Cl• and Cl_2 are also liberated in high yields and this increases rates of iodide oxidation.[10] The rate of triiodide formation is easily monitored spectrophotometrically. For many years, this so-called Weissler reaction has remained the standard dosimeter for sonochemical reactions.

The recent advent of commercially available high-pressure jet fluidizers capable of pressure drops as high as 2 kbar and jet velocities approaching 200 m/s has led to numerous applications in the physical processing of liquids, for emulsification, cell disruption, etc. Chemical consequences of such processing, however, have received little examination. One important exception comes from W. R. Moser and co-workers,[11] who have shown that such a device can be utilized to prepare nanostructured catalytic materials. Moser speculated that the unusual properties of his catalysts resulted from hydrodynamic cavitation within the fluidizer.[11] We describe here conclusive experimental evidence for chemical reactions caused by hydrodynamic cavitation within a jet fluidizer.

In a typical run,[12a] 60 mL of 1.0 M KI in purified water saturated with carbon tetrachloride was introduced at a constant flow rate into the Microfluidizer with a liquid pressure of 1.24 kbar. The reaction solution temperature increased 10 to 12 °C within 90 s and stabilized at the temperatures reported herein. Aliquots (4 mL) of the processed solution were periodically extracted from the reaction system by airtight syringes, analyzed spectrophotometrically, and returned to the reservoir after analysis. The rate of I_3^- formation was calculated from the change in absorbance at 353 nm ($\epsilon = 26\,400$ M^{-1} cm^{-1})[12b] as a function of reaction time. Initial studies conducted with Ar-sparged water gave relatively low rates of I_3^- production; saturation of the Ar sparged H_2O with CCl_4 resulted in a 20-fold increase in I_3^- production, as has been typically observed for ultrasonic cavitation.[10] This is attributed to ready formation of Cl• and Cl_2 from CCl_4 under cavitation conditions.

The effect of upstream liquid pressure on the rate of I_3^- production was investigated over the range 100–1500 bar. The reaction rate increases linearly with liquid pressure (Figure 1), but with a threshold pressure of 150 bar. Below 150 bar of hydrostatic pressure, no chemical reactions were observed; this probably represents the minimum jet velocity necessary to induce cavitation. The resistance of a turbulent flow to cavitation is given by its cavitation number σ, as defined in eq 1:[6]

$$\sigma = \frac{p_d - p_v}{p_u - p_d} \approx \frac{p_d}{p_u} \qquad (1)$$

where p_d, p_u, and p_v are the downstream, upstream, and vapor pressures, respectively, and the approximation holds when $p_u \gg p_d \gg p_v$, as they do under our experimental conditions. An increase in upstream pressure should decrease σ and increase the number of cavitation events. This in turn should increase the rate of I_3^- formation, if the chemistry is cavitation driven, consistent with our observations.

The conditions formed during *acoustic* cavitation and consequently sonochemical rates are known to be affected both by the polytropic ratio of the dissolved gas (i.e., $\gamma = C_p/C_v$,) and by the thermal conductivity of the dissolved gas. The former parameter determines the temperature achieved during bubble compression, and the latter is responsible for heat dissipation from the collapsing bubble to the surrounding solution. In the present study using Ar/He mixtures, the γ of the dissolved gas was fixed at 1.67, while the thermal conductivity was varied from 0.017 to 0.142 W m^{-1} K^{-1}. As shown in Figure 2, the I_3^- formation rate decreases exponentially as the thermal conductivity of the dissolved gas increases. This observation is best explained in terms of the hot-spot model for cavitation which suggests that the maximum temperature (T_{max}) realized

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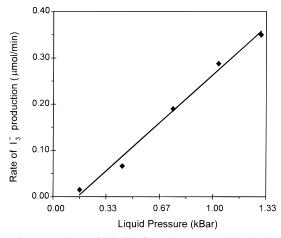(6) Knapp, R. T.; Daily, J. W.; Hammitt, F. G. *Cavitation*; McGraw-Hill: Inc.: New York, 1970.
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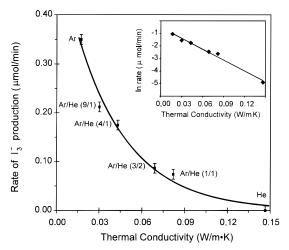(8) Anbar, M. *Science* **1968**, *161*, 1343.
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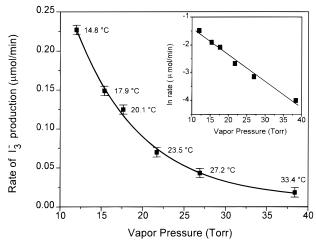
Figure 1. Dependence of triiodide formation rate on the hydrodynamic pressure used to induce cavitation. Conditions: 60 mL of 1 M KI solution in CCl$_4$-saturated water was recycled under static Ar atmosphere at a constant reaction temperature of 12 °C.

Figure 2. Dependence of triiodide formation rate on the nature of the dissolved gas during hydrodynamic cavitation. Conditions: 60 mL of 1 M KI solution in CCl$_4$-saturated water was recycled under static Ar or Ar/He atmosphere at a constant reaction temperature of 12 °C and liquid pressure of 1.24 kbar.

Figure 3. Dependence of triiodide formation rate on bulk temperature and on solvent vapor pressure during hydrodynamic cavitation. Conditions: 60 mL of 1 M KI solution in CCl$_4$-saturated water was recycled under static Ar atmosphere at liquid pressure of 1.24 kbar.

pressure. This same dependence is seen in sonochemical reactions and is attributed to the increase in polyatomic vapor inside the bubble before collapse, which decreases γ and cushions the collapse of the cavitating bubble.[15] While it is difficult to make direct comparisons of energy efficiency (e.g., moles of product per kilowatt hour of electrical energy), acoustic cavitation provides significantly higher rates for the Weissler reaction, at least for the specific source of hydrodynamic cavitation tested here.

In summary, we have demonstrated that the chemical effects of hydrodynamic cavitation and acoustic cavitation respond identically to experimental parameters, notably the bulk temperature and the nature of the dissolved gas. In particular, the rates decrease with increasing solution temperature, due to the increased solvent vapor pressure inside the bubble; increasing solvent vapor pressure attenuates the efficacy of cavitational collapse, the maximum temperature reached during such collapse, and, consequently, the rates of cavitational reactions. By reducing the adiabaticity of bubble collapse, the thermal conductivity of the dissolved gas also has a substantial effect on the maximum temperature achieved inside a cavitating bubble; increased thermal conductivity decreased rates of cavitation reactions.

in a collapsing bubble decreases linearly with increasing thermal conductivity of the entrapped gas.[13] This inverse relationship of T_{max} to the thermal conductivity of dissolved gases should lead to an exponential decrease in the I$_3^-$ formation rate (assuming Arrhenius behavior) with increasing thermal conductivity, as observed.

The influence of bulk solution temperature on the I$_3^-$ production rate was investigated to probe the effect of vapor pressure. The I$_3^-$ production rates decrease sharply with increasing temperature, as shown in Figure 3. This same behavior has been reported for many previous *acoustic* cavitation studies.[10b,14,15] Figure 3 also demonstrates that the observed rates decrease exponentially with increasing solvent vapor

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