The Sonochemical Hot Spot

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Sonochemistry, the chemical effects of ultrasound, is an area of increasing interest to chemists. The principle mechanism of sonochemistry is transient cavitation [1-3]. During transient cavitation, small bubbles are created, grown, and violently collapsed, which creates localized "hot-spots" in which temperatures and pressures are postulated to be extremely high [3].

Although sonochemistry has been used extensively in research and industry, the exact site of reactivity is unknown. To probe this question, a series of experiments using the sonochemical reactions of four metal carbonyls [4] were studied as dosimeters [5-8].

$$\mathrm{Fe(CO)_5} \xrightarrow{)))} \mathrm{Fe(CO)_n + nCO}$$

$$\mathrm{Fe(CO)_3 + 2Fe(CO)_5} \longrightarrow \mathrm{Fe_3(CO)_{12} + CO}$$

$$\mathrm{M(CO)_6 + L} \xrightarrow{)))} \mathrm{M(CO)_{6-n}L_n} \quad \text{(where M = Cr, Mo, or W)}$$

In these experiments, the observed first-order rates of CO dissociation were determined as a function of metal carbonyl vapor pressure. Results indicate that as metal carbonyl vapor pressure increases so does the observed sonochemical rate. This corresponds to a vapor pressure dependent reaction occurring within the gas-phase inside the collapsing cavity. When the data are extrapolated to zero vapor pressure, a finite rate still exists. This corresponds to a vapor pressure independent reaction occurring in the thin liquid shell immediately surrounding the collapsing cavity. Therefore, there are two sites of sonochemical reactivity, a gas-phase and a liquid-phase site.

Although cavitation is well understood qualitatively, quantitative determination of the conditions occurring during cavity collapse are few. Early hydrodynamic models have been proposed temperatures of 10,000 K and pressures of 10,000 atm [9]. Later models have predicted temperatures of 2000 K and 1000 atm [10]. Experimental determination of conditions during collapse is lacking. Using the relative slopes and intercepts of the metal carbonyl dosimeter dissociation reactions, activation parameters (A and E_a) for CO dissociation from gas-phase laser pyrolysis [11], and comparative rate thermometry from shock tube chemistry [12], estimates of the maximum effective temperatures reached during cavity collapse were made. In comparative rate thermometry, the effective temperature of two chemical processes occurring under identical conditions can be determined by using the Arrhenius equation.

$$\ln (A/k) = (1/RT)\, E_a$$

The maximum effective temperatures were calculated to be 5200 K for the gas phase and approximately 1900 K for the liquid phase at 5.0 torr total system vapor pressure.

Temperatures and pressures reached during cavitational collapse have applications to synthetic chemistry. One such application is olefin epoxidation which is a very important industrial process [13]. In a typical industrial epoxidation, olefin and an organic hydroperoxide react to form primarily epoxide and allylic products. Cyclic olefins, in the presence of mixed metal catalysts, undergo autoxidation [14]. In these reactions, cyclic olefins react to form hydroperoxide which further reacts with more olefin to form epoxide and allylic alcohol.

Ultrasonic irradiation of cyclohexene containing $Mo(CO)_6$ forms epoxide and allylic products in a 1:1 ratio. The effects of catalyst-type, catalyst concentration, cyclohexane concentration, and O_2 concentration were studied. In addition, a sonochemical mechanism has been proposed.

References

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