Ultrasonic Emulsification of Liquid, Near-Critical Carbon Dioxide−Water Biphasic Mixtures for Acceleration of a Hydrolysis Reaction

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A surfactant-free method based on power ultrasound was used to emulsify biphasic mixtures of liquid, near-critical carbon dioxide and water ($T = 30$ °C, $P = 80$ bar). When ultrasound above a threshold power density (roughly 0.15 W/cm^3 at 20 kHz) was applied to a biphasic system of carbon dioxide and water, emulsions were formed which remained turbid for approximately 30 min (after 2 min of continuous ultrasound). Pulsed ultrasound (20% duty of a 2.5 s cycle at 20 kHz) could be used to maintain the emulsions indefinitely. Benzoyl chloride hydrolysis was selected as a model chemical reaction because of its rapid rate in pure water and the relative insolubility of the aroyl halide in the aqueous phase as compared to the carbon dioxide phase. The kinetic rate was measured under a range of ultrasonic pulsed power densities and zero ultrasound (i.e., silently) as a control. The measured, apparent, first-order rate constant was accelerated 100-fold in the presence of ultrasound at 0.50 W/cm^3 relative to silent conditions. The accelerative effect of ultrasound saturates with increasing power beginning at 0.50 W/cm^3. These results demonstrate the use of power ultrasound to create liquid carbon dioxide−water emulsions that, without surfactants or other additives, accelerate hydrolysis of substrates with low water solubility.

Near-critical and supercritical carbon dioxide ($scCO_2$) has many physicochemical properties (high diffusivity, low viscosity, and tunable density) which make it an attractive solvent for chemical processing and/or reactions on an industrial scale. Other advantages over conventional solvents are that it is inexpensive, nontoxic, and nonflammable. It is not surprising, therefore, that both near-critical and supercritical carbon dioxide ($T_c = 31.1$ °C, $P_c = 73.8$ bar), have been used on an industrial scale for a number of processes, most notably extractions.[1] Despite this success, relatively little progress has been made toward using carbon dioxide as a solvent for chemical reactions with the exception of select polymerization reactions. The literature suggests two reasons for this. First, carbon dioxide exhibits poor solvent power for many reagents of interest[1] including most hydrophilic compounds and high molecular weight hydrocarbons. Second, though many studies have demonstrated some tunability of reaction rates and/or selectivity as a function of fluid density,[2−11] there are few examples of dramatic improvements in productivity in supercritical fluids as compared to traditional organic solvents. Without significant technological advantages, industrial implementation of “greener” technologies such as replacement of organic solvents by $scCO_2$ will continue to be slow.

In an effort to improve either selectivities or rates of certain reactions in $scCO_2$, a number of researchers have turned to heterogeneous and homogeneous catalysts. Initial development of homogeneous catalysis was delayed by the low solvent power of carbon dioxide for common catalysts, but the discovery that the addition of CO_2-philic ligands (primarily fluorinated alkanes and ethers or siloxane-based molecules) could increase the solubility of many transition-metal-based organometalic compounds has opened the field of supercritical-fluid-based homogeneous catalysis.[12−20] Unfortunately, these otherwise promising catalysts are more expensive than their lipophilic analogues. Additionally, like all homogeneous catalysts, carbon dioxide-based homogeneous catalysts must be separated from the product postreaction mixture, which can be difficult or expensive. Heterogeneous catalysts, on the other hand, can be easily recovered and recycled; their disadvantages are their lower specificity as compared to homogeneous catalysts and potential for mass transport limitations (both in the bulk fluid and within the catalyst support structure).

Because of these limitations, techniques that exploit the advantages of reactivity inherent to homogeneous catalysts while retaining the ease of separation of heterogeneous catalysts are of great interest. One approach has been to employ a homogeneous catalyst which is phase-separated from the reactants and products,[21−23] either by immobilization on a solid support or by dissolution in a second, CO_2-immiscible, liquid phase. Although supporting homogeneous catalysts on heterogeneous supports is a viable approach, this solution does not address the solubility limitations of $scCO_2$. Use of CO_2 with another solvent is intriguing because a judicious choice of the second solvent would allow for solubilization of a wide range of chemical reagents. The combination of liquid water and $scCO_2$ (which are essentially immiscible close to the critical point of pure CO_2) is particularly attractive. Since the two solvents have complementary solvent powers, their combination suggests the ability to solubilize a wide range of reagents and should facilitate liquid−liquid phase segregation of reactants and products from homogeneous catalysts. In addition to addressing the disadvantages of conventional homogeneous catalysis, this approach preserves the environmental advantages of carbon dioxide since the only additives are water and an easily recoverable catalyst.

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One disadvantage to phase segregation is that it increases mass transport resistances, as the reagents need to enter the phase containing the catalyst prior to reacting. To decrease mass transport resistance in phase-segregated systems, high-surface-area emulsions and microemulsions of carbon dioxide and water have been investigated.[24−29] The use of microemulsion/emulsions shows promise, but stabilization of water/carbon dioxide interfaces generally requires specially fluorinated surfactants. The use of these surfactants has economic and environmental impacts, which may prohibit some commercial applications. Furthermore, addition of any surfactant (fluorinated or not) to pure carbon dioxide/water systems necessarily detracts from their chemically benign natures and complicates otherwise simple chemistry as well as postreaction separations. Practical implementation of water/carbon dioxide microemulsion systems would be accelerated greatly by a surfactant-free means of emulsification.

This paper describes a novel approach to this end. Our approach, which requires no chemical additives, utilizes ultrasound to dynamically mix and emulsify the liquid water and liquid, near-critical carbon dioxide. More specifically, the results indicate that, above a certain threshold power density, ultrasound is an efficient means of emulsifying liquid water and near-critical carbon dioxide mixtures to achieve intimate contact between the two liquid phases. More importantly, the rate of a carefully chosen model reaction (hydrolysis of benzoyl chloride) was measured and shown to be substantially accelerated by sonication. These experiments provide the information necessary to develop more complicated catalyzed schemes. The remainder of this paper describes the results in more detail.

All experiments were conducted in a custom-designed and built reactor consisting of two intersecting cylindrical chambers (1.9 cm i.d.) bored in a slab (22.9 cm × 15.2 cm × 7.6 cm) of 316-stainless steel. Three of the four apertures contain α-Al_2O_3 sapphire windows sealed with stainless steel glands. The fourth aperture contains a titanium sonic probe (0.80 cm o.d., Sonics and Materials, Inc.) sealed with a stainless steel gland. The sonic processor was a Branson Sonifier 450. The internal volume of this reactor was measured as 87.2 ± 0.4 cm^3, and its maximum design operating pressure was 250 bar (at $T = 50$ °C). The reactor was equipped with a pressure transducer (Dynisco, 8322) and a T-type thermocouple. Reactor temperature was maintained by a PID controller (Omega, 9001CN) and thermal tape wrapped around the vessel walls. The reactor and acoustic equipment are described in greater detail elsewhere.[30,31]

Panels a−c of Figure 1 are photographs which compare the behavior of carbon dioxide/water mixtures (30 °C/75 bar/50% water by volume) before application of ultrasound (a) and during irradiation with continuous ultrasound at power densities of (b) 0.11 or (c) 0.55 W/cm^3.[32] Panels d−f of Figure 1 are idealizations of the photographic images which are provided to highlight the most important features. At a power density of 0.11 W/cm^3, the interface experiences deformation in the form of surface waves but no emulsion is formed (Figure 1b,e). Above approximately 0.16 W/cm^3, application of ultrasound generates emulsions within several seconds. There is a relatively sharp threshold power density, below which emulsification is not observed and above which emulsification is quite facile. Turbidity measurements taken after 2 min of continuous sonication at various power densities illustrate this threshold-emulsification power density. Figure 2 is a plot of the ratio of the intensity of light transmitted by the emulsion (I) to that transmitted by the unmixed, biphasic system (I_0). For the three data sets representing sonication at power densities greater than or equal to 0.16 W/cm^3, the turbidity is initially high and slowly diminishes over a period of 30 min. The data set representing sonication at 0.05 W/cm^3 exhibits high initial turbidity, but the incremental attenuation of light rapidly decays to nearly zero (i.e., $I/I_0 = 1$). The presence of some turbidity after termination of the ultrasound at 0.05 W/cm^3 is due the formation of surface waves at the carbon dioxide/water interface (as shown in Figure 1b,e) which subsequently scatter incident light and to the deposition of large (1 mm) droplets of water on the sapphire windows. The surface waves rapidly relax and the turbidity diminishes substantially within 2−3 min. The large droplets detach more slowly, resulting in slight attenuation of the incident light for approximately 10 min. At power densities of 0.16 W/cm^3 and greater, the carbon dioxide−water system becomes extremely turbid following sonication. The persistence of extreme turbidity for several minutes following termination of sonication is indicative of the formation of tiny droplets of the

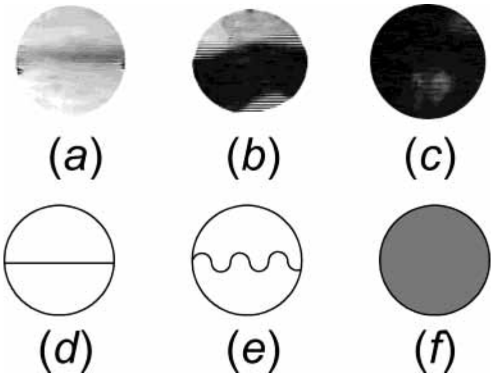

Figure 1. Images of reactor contents (a) prior to sonication, (b) during sonication at 0.11 W/cm^3 of sonic power density, and (c) during sonication at 0.55 W/cm^3 of power density. Images labeled d−f are schematic representations of phase separation and mixing which correspond to panels a−c of Figure 1, respectively. In all images the carbon dioxide-continuous emulsion is the less dense emulsion (i.e., the carbon dioxide emulsion is the upper phase). Experimental conditions were 30 °C, 75 bar, and 50% water by volume.

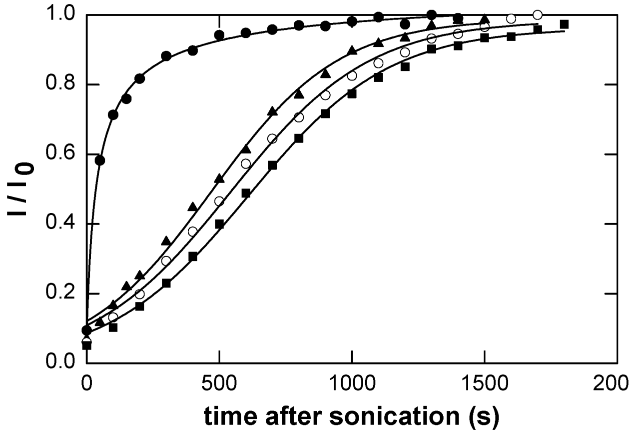

Figure 2. Turbidity of reactor contents after 2 min of continuous sonication. The ordinate (I/I_0) is the attenuation of light (500 nm) from a fiber optic source (Fostec, 8375). The optical path length through the reactor was 12 cm. Conditions were 30 °C, 75 bar, and 50% water by volume. All samples were sonicated continuously for 2 min prior to the reported turbidity measurements: ●, 0.05 W/cm^3; ▲, 0.16 W/cm^3; ○, 0.26 W/cm^3; ■, 0.55 W/cm^3. Sonication at less than 0.16 W/cm^3 did not form emulsions; however, the ability to emulsify the system saturated with sonic powers greater than 0.16 W/cm^3. Within the limits of experimental reproducibility, sonication at powers greater than 0.16 W/cm^3 did not produce emulsions with either greater initial turbidities or longer lifetimes. All emulsions broke in less than 30 min.

two phases which have been dispersed throughout the reactor. Panels c and f of Figure 1 are respectively photographs and schematic representations of this condition. Additionally, Figure 2 shows that increasing the power density beyond the threshold required for emulsification has little benefit; emulsions formed at power densities greater than 0.22 W/cm^3 are neither significantly more turbid (immediately after termination of sonication) nor more stable (i.e., they take no longer to break, within the limits of experimental reproducibility) than those formed at lower power density. In the presence of pulsed ultrasound (0.5 s ON/2.0 s OFF, i.e., 20% duty of a 2.5 s cycle) at pulse power densities greater than 0.15 W/cm^3, emulsions persisted with no apparent change for as long as the ultrasound was applied (i.e., for as much as several hours). Ultrasound simultaneously generated emulsions with both near-critical carbon dioxide and liquid water continuous phases at all conditions investigated. Both types of emulsions broke completely within 30 min after termination of the ultrasonic irradiation, as demonstrated by the turbidity plots in Figure 2. This spontaneous and rapid breaking after the termination of ultrasonic agitation is expected to facilitate postreaction separations of products.

To probe mass transport conditions in this hybrid environment, the rate of the hydrolysis of benzoyl chloride to benzoic acid was measured at 30 °C and 75 bar. This reaction was selected for several reasons. First, benzoyl chloride is virtually water insoluble but is highly CO_2 soluble. Conversely, benzoic acid is preferentially solubilized by water (roughly 10:1 in molar units at experimental conditions[33]). An analysis of the literature data for this reaction indicates that the hydrolysis will be confined primarily to the water phase. The reported intrinsic rate constant for benzoyl chloride hydrolysis in pure water (k_{int}) is approximately $1.0 \pm 0.5\ s^{-1}$ (25 °C, 1 bar).[34−38] The reported apparent first-order rate constant in dioxane/water mixtures (with a water concentration of ~1 M) is much lower $\sim 4 \times 10^{-5}\ s^{-1}$.[39] If one accounts for differences in the water concentration (i.e., 55 M as compared to 1 M), the true second-order rate constant for benzoyl chloride hydrolysis in the nonpolar dioxane mixture is roughly 1000 times smaller than that in pure water. On the basis of its low dielectric constant[40] (approximately 1 as compared to roughly 78 for liquid water at room temperature), CO_2 should also be an extremely poor solvent for this hydrolysis. Thus, to a good approximation, the hydrolysis reaction occurs only in the water phase, after transport of the benzoyl chloride through the CO_2 phase. The rapid hydrolysis of benzoyl chloride in the water phase ensures that, under most circumstances, transport of the benzoyl chloride (in either the carbon dioxide or water phase) will in fact be a rate-limiting step. The importance of mass-transport barriers in the benzoyl chloride hydrolysis makes it a satisfactory choice as a model for more complicated schemes involving homogeneous catalysis for which extremely fast chemical kinetics are expected. A final, though quite important, reason for selecting this model reaction is that a convenient benchmark exists in the literature for hydrolysis of benzoyl chloride in a water/carbon dioxide microemulsion.[28]

Hydrolysis kinetics[41] were measured without ultrasound (i.e., under silent conditions) and under conditions of pulsed ultrasound (20% duty of a 2.5 s cycle at 20 kHz) from 0.05 to 0.77 W/cm^3. Under all conditions, the rate of disappearance of benzoyl chloride was described adequately by apparent first-order kinetics, as depicted in Figure 3. The slopes of the first-order plots of Figure 3 are interpreted as the observed first-order rate constant (k^*). As can be seen in Figure 4, the magnitude of k^* increased very significantly from its silent value of about $1 \times 10^{-5}\ s^{-1}$ with application of even low power ultrasound intensities (less than 0.11 W/cm^3). Above about 0.50 W/cm^3, the ultrasonic effect saturates at a value of $1 \times 10^{-3}\ s^{-1}$, i.e., 2 orders of magnitude greater than the silent value. The value of k^* at saturation is also much greater than the reported rate constant[28] for hydrolysis of benzoyl chloride in a water/carbon dioxide microemulsion (the fastest reported value was $5 \times 10^{-5}\ s^{-1}$). The fact that the sonicated rate is roughly 1000-fold slower than the intrinsic rate in pure water is indicative of the preferential partitioning of benzoyl chloride into the carbon dioxide phase. Increasing the power density of the ultrasound beyond 0.50 W/cm^3 had no effect on the observed rate. This finding is similar to that demonstrated in the turbidity plots of Figure 2.

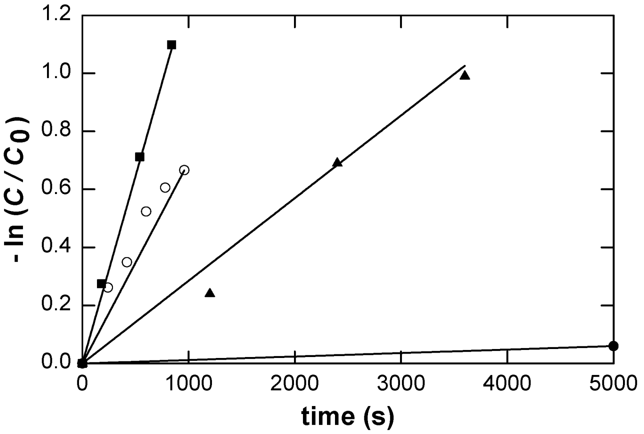

Figure 3. Observed first-order plots for the hydrolysis of benzoyl chloride in carbon dioxide/water systems as a function of power density (pulsed ultrasound, 20% duty of a 2.5 s cycle, 20 kHz) for representative runs: ●, 0.0 W/cm^3 (i.e., silent conditions); ▲, 0.10 W/cm^3; ○, 0.25 W/cm^3; ■, 0.75 W/cm^3. Conditions were 30 °C, 75 bar, and 50% water by volume.

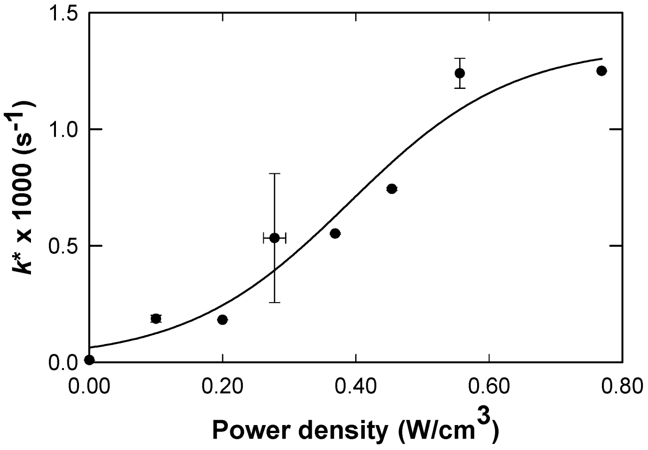

Figure 4. Observed first-order rate constant (k^*) for benzoyl chloride hydrolysis as a function of sonic power. The observed rate constant increases strongly at low sonic power density and saturates at sonic power densities greater than 0.50 W/cm^3. Conditions were 30 °C, 75 bar, and 50% water by volume. Ultrasound was pulsed at the indicated instantaneous power density with a duty of 20% (2.5 s cycle). Error bars represent the estimated standard deviation of the population based on three runs. The line is an empirical fit, and no physical basis is intended.

Mechanical agitation, induced either by a magnetically coupled, Teflon-coated, stir bar or by recirculation of the water phase by a secondary pump (20 mL/min), had no effect on the observed rate constant under silent conditions at short times ($t < 12$ h). For $t > 12$ h, greater conversion to benzoic acid was measured in agitated systems. For the silent case, experiments were conducted using different positions of the water sampling point to ensure that samples were representative.

The observation of a threshold power density, below which sonication has little effect on emulsification, has been observed in a number of acoustically activated chemical systems[42] and is generally attributed to the minimum power density required to cavitate the liquid. Alternatively, in this high-pressure[43] system, the threshold power density may be related to the minimum power density required to drive surface waves at the carbon dioxide/water interface into an unstable regime. Here, low power densities of sonication increase the rate 10-fold, most likely due to extremely efficient mixing of the interfacial region by the formation of surface waves. Further acceleration at higher power densities is due to emulsification either by cavitation, wave breaking, or a combination thereof. The saturation of the sonic effect is also analogous to results observed for sonication of more conventional systems. In such cases, the saturation effect is generally attributed to screening of the bulk of the fluid by intense cavitation in the immediate vicinity of the ultrasound source.[42] A similar effect may influence the results reported here.

Our hypothesis is that the accelerative effect of ultrasound is primarily due to enhanced mass transport and not to sonochemical effects. A first-order analysis of sonochemical rate phenomena and of transport behavior support this hypothesis. A large body of empirical evidence[42] for reactivities for homogeneous reactions has shown that rate constants are generally increased by a multiple of 2 or less under sonochemical conditions, unless the system is cooled to temperatures less than room temperature. This is particularly true for reactions which take place via ionic pathways, such as the hydrolysis of benzoyl chloride. The 2 order of magnitude acceleration reported in this study is considerably greater than that typically observed. Furthermore, ultrasonic emulsification of water and oil mixtures has been extensively studied and the results provide further evidence that the primary mechanism for the rate accelerations observed in this study is transport enhancement. In all instances[44−47] and for a wide range of systems and conditions, droplet diameters considerably less than 10 μm are reported. In some instances, with the aid of surfactants, submicrometer droplets can be generated.[46] For a water droplet in a continuous carbon dioxide phase, a representative length scale for benzoyl chloride mass-transport penetration is $(D_{ab}/k_{int})^{1/2}$, where D_{ab} is the diffusion coefficient for benzoyl chloride in water and k_{int} is the intrinsic rate constant for benzoyl chloride hydrolysis in pure water. If D_{ab} is roughly 1×10^{-5} cm^2/s for diffusion of benzoyl chloride in water,[48] the length scale for benzoyl chloride penetration into the water droplet is 10 μm, which is similar to the expected droplet diameter in the emulsion. For the water continuous emulsion, the length scale for penetration of benzoyl chloride from the carbon dioxide droplet into the bulk water phase is still $(D_{ab}/k_{int})^{1/2} \sim 10\ \mu$m. The relevant length scale for the bulk water phase is now the distance between neighboring water droplets which can be roughly approximated as the diameter of the carbon dioxide droplets (i.e., less the 10 μm). In both emulsified cases, therefore, the concentration of benzoyl chloride in the water phase is nearly uniform and equal to the concentration at the water/carbon dioxide interface. By comparison, under silent conditions, only a small fraction of the water phase is utilized for reaction. The acceleration of hydrolysis upon sonication corresponds to an overall reduction of mass transport resistance by dramatically increasing the interfacial contact area between the CO_2 and water phases such that a much greater fraction of the water phase is utilized for the reaction.

These results show the potential for using ultrasonic emulsification of carbon dioxide/water mixtures for synthetic chemistry. Work in progress in our laboratory is focused on gaining a better understanding of the emulsification process (including both the formation mechanism(s) and general emulsion characterization) while expanding applications of our approach to other synthetic reactions and aqueous extractions. Future publications will investigate the interplay between mass transport, reaction kinetics, and reagent partitioning in a quantitative manner[31] and demonstrate the utility of our approach for chemical reactions of greater synthetic interest.[49]

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$$\frac{C}{C_0} = \frac{C_{\text{benzoyl chloride at time } t}}{C_{\text{benzoyl chloride initial}}} = \frac{n_{\text{benzoyl chloride initial}} - n_{\text{benzoic acid at time } t}}{n_{\text{benzoyl chloride initial}}}$$

where n refers to the number of moles of a given analyte and the volume of the reactor is a constant and cancels out of the relationship. Mass balance closure was confirmed to within ±10% for all experiments by completing the reaction and analyzing the mixture for benzoic acid content. All reactions were conducted under two-phase conditions as was verified visually.

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