

Organic Synthesis in Water/Carbon Dioxide Emulsions

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The synthetic reaction between a hydrophobe, benzyl chloride, and a hydrophilic nucleophile, KBr, is reported in water-in-carbon dioxide (w/c) and carbon dioxide-in-water (c/w) emulsions. Emulsions containing equal amounts of water and CO₂ were formed with both anionic perfluoropolyether ammonium carboxylate (PFPE COO⁻NH₄⁺) and nonionic poly(dimethylsiloxane)-*g*-poly(ethylene oxide) and poly(butylene oxide)-*b*-poly(ethylene oxide) surfactants, without the need for any added cosolvent. Higher yields of benzyl bromide were obtained in w/c and c/w emulsions (41–47%) as compared to water-in-octane emulsions (33%). Yields were much higher than in a previous study of the same reaction in a w/c microemulsion (Jacobson et al. *J. Org. Chem.*, following paper in this issue), since the much larger amount of water in the emulsion allowed for a greater excess of KBr.

Introduction

A unique feature of near-critical and supercritical fluids such as CO₂ is that the density and likewise the solvent strength may be tuned with pressure or temperature to manipulate phase behavior and rates and selectivities of chemical reactions.^{1,2} Unfortunately, CO₂ is a very weak solvent, similar to that of fluorocarbons, because of its low cohesive energy density. However, with the addition of surfactants, polar nonvolatile substances, such as ions, may be dissolved in CO₂.³

In microemulsions and emulsions composed of water and supercritical fluids, both hydrophilic and hydrophobic compounds may be dissolved without requiring an organic solvent. Microemulsions are thermodynamically stable and optically transparent, with typical drop diameters of 2–50 nm. With surfactants, turbid emulsions may be stabilized kinetically with droplet diameters in the range of 0.5–10 μm. In both cases, the high interfacial area may be used to facilitate chemical reactions between a hydrophobic substrate and a hydrophilic reactant, such as a nucleophile, at the interface.

The formation of w/c microemulsions was reported recently for a hydrocarbon–fluorocarbon hybrid ionic surfactant⁴ and a perfluoropolyether ammonium carboxylate (PFPE COO⁻NH₄⁺)³ surfactant. In both cases the size of the microemulsion droplets was determined by neutron scattering.^{5,6} In a complementary paper to this

study, we demonstrated synthetic organic reactions in H₂O/CO₂ (w/c) microemulsions.⁷ For similar substrate concentrations, product yields in the w/c microemulsions were comparable to or even greater than those obtained in the w/o microemulsions. The relatively small amount of water in this system limits the amount of a hydrophilic reactant, e.g., potassium bromide, that may be dissolved in these microemulsion droplets. Larger amounts of water may be dispersed in CO₂ by forming emulsions instead of microemulsions.

The interfacial tension, γ , between H₂O and CO₂ is on the order of 20 mNm⁻¹ at pressures above 70 bar,⁸ much lower than that between H₂O and alkanes (30–50 mNm⁻¹). This lower γ reflects the fact that CO₂ is more miscible with water than are alkanes, because of its acidity and quadrupole moment. To achieve low values of γ required to form emulsions, less surfactant may be required for CO₂ than for alkane continuous phases, since γ without surfactant starts out so much lower.

With the use of various surfactants with PFPE, poly(dimethylsiloxane) (PDMS), and poly(alkylene oxide) tails, the interfacial tension between water and CO₂ may be reduced to approximately 1 mNm⁻¹,⁸ which is sufficiently low for forming emulsion droplets on the order of microns. Recently, milky-white kinetically stable emulsions have been formed for equal amounts of water and carbon dioxide which filled essentially the entire volume of the high-pressure vessel.^{9,10} These emulsions were formed with surfactants composed of PFPE, PDMS, or poly(butylene oxide) tails. In many cases these emulsions with surfactant concentrations ranging from 0.1 to 1 wt % were stable for days.

Our objective is to evaluate the efficacy of w/c and c/w emulsions for reactions between water-insoluble organic substrates and water-soluble nucleophiles. Here we consider the nucleophilic substitution reaction between

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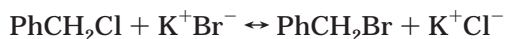
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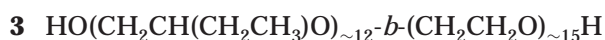
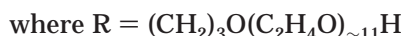
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benzyl chloride and potassium bromide



Even though the area/volume is higher for a microemulsion droplet than an emulsions droplet, the volume fraction of water can be much larger for the emulsion. Consequently much larger amounts of KBr may be introduced in the emulsion compared with the microemulsion. We compare the product yield of benzyl bromide for reactions in w/c and c/w emulsions formed with the anionic surfactant $\text{CF}_3\text{O}(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_3\text{CF}_2\text{COO}^-\text{NH}_4^+$ (PFPE $\text{COO}^-\text{NH}_4^+$) **1** and the nonionic surfactants poly(dimethylsiloxane)-*g*-poly(ethylene oxide) (PDMS-*g*-PEO) **2** and poly(butylene oxide)-*b*-poly(ethylene oxide) (PBO-*b*-PEO) **3**. The results for the emulsions are compared to those for a w/o emulsion stabilized by the anionic surfactant bis(2-ethylhexyl) sodium sulfosuccinate (AOT) **4**, where *n*-octane is the oil phase.



Very low specific conductivities in the range of 20 $\mu\text{S}/\text{cm}$ were measured for emulsions stabilized by **1** with equal amounts of water and CO_2 , indicating that water is the dispersed phase (w/c emulsion).⁹ In contrast, c/w emulsions with high conductivities are formed for **3**.¹⁰ The emulsion type is unknown for **2**, but we have been able to form both w/c and c/w emulsions for similar surfactants composed of PDMS and PEO.

The nature of the H_2O – CO_2 interface is likely very different than that of a water–alkane interface due to the lower γ for the former and the small size and low viscosity of CO_2 . With the low viscosity for this interface and the high diffusion coefficients in the CO_2 phase, it is conceivable that heterogeneous reactions may occur faster in w/c and c/w emulsions than in w/o emulsions.

Although numerous studies of organic reactions have been reported in microemulsions,¹¹ extremely few have been reported in emulsions,^{12,13} with the exception of heterogeneous polymerizations. The difficulty in breaking an emulsion after reaction is a formidable problem. For w/c and c/w emulsions, the emulsion may be broken rapidly simply by reducing the pressure to separate the water and CO_2 phases. The low solubility of water in CO_2 is well-known.¹⁴ In supercritical fluids, the density of the fluid, which may be adjusted with temperature and pressure, has a large effect on the solvation of the

surfactant tail^{15,16} and thus the phase behavior and stability of the emulsion, as has been studied for microemulsions.^{17,18}

Experimental Section

General. AOT (bis(2-ethylhexyl) sodium sulfosuccinate) was obtained from Aldrich and used as received after drying under vacuum at 60 °C for at least 10 h. Benzyl chloride, potassium bromide, anisole, naphthalene, and *n*-octane were all obtained from Aldrich and used without any further purification. PBO-*b*-PEO (SAM-185, ca. 1500 g/mol) was purchased from PPG Industries and PDMS-*g*-PEO (2758 g/mol) was synthesized as described previously.¹⁹ The PFPE $\text{COO}^-\text{NH}_4^+$ (940 g/mol) was a gift from Ausimont, synthesized according to published procedures.²⁰ All three surfactants were used as received. Instrument grade carbon dioxide (Proxair Inc.) was purified with an oxytrap (Oxyclear model no. RGP-31-300, Labclear, Oakland, CA.). Nanopure II water (Barnstead, Dubuque, IA) was used in all experiments. Product mixtures were analyzed by GC in exactly the same manner as before.⁷

High-Pressure Apparatus. The reactions were performed in the same apparatus as before⁷ with the following modifications. A reciprocating minipump (Thermo Separations Products) with a maximum flow rate of 460 mL/h was used to continuously recirculate the emulsion from the bottom of the reaction cell through a 6-port 2-position valve (C6W, Valco Instruments Co., Inc., Houston, TX) equipped with a 100 mL sample loop and back into the reaction cell through a capillary (i.d. = 254 μm , l = 5 cm). This design allowed samples to be taken throughout the reaction process and also produced the high shear necessary to form the emulsion in the cell by spraying the lower aqueous phase into the upper CO_2 phase. At the desired sampling time the sampling valve was switched and the sample was trapped in ca. 500 μL of ethanol.

Low-Pressure Experiments. The experiments for the $\text{H}_2\text{O}/n$ -octane system at atmospheric pressure, with or without AOT, were performed in a stainless steel autoclave (Parr, 300 mL) equipped with a mechanical mixer and a stainless steel stirring blade.

Synthesis of Benzyl Bromide. The emulsion was made with equal weights of water and CO_2 or *n*-octane. Typically, the cell was loaded with 6 g of H_2O , 60 mg (0.5 wt % based on total weight of H_2O and CO_2 or oil phase) of surfactant (or 0.1 wt % in the case of PDMS-*g*-PEO), and an internal standard. Potassium bromide (1.428 g) was added to give a 2 M concentration in the H_2O phase ($V \sim 6$ mL). The cell was then closed and filled with 6 g of CO_2 (or *n*-octane) and pressurized to the desired reaction pressure. After the reaction cell was heated and an emulsion had formed, benzyl chloride was injected with the 6-port valve to give a concentration of 110 mM in the CO_2 (or *n*-octane) phase (e.g., in the case of CO_2 , 6 g = 7.607 mL at 65 °C and 4000 psi, and 96.3 mL of benzyl chloride was injected). The reaction was monitored by taking out aliquots of sample with the sample loop in the 6-port valve and analyzing them by GC.

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Table 1. Yield (%) of Benzyl Bromide as a Function of Oil Phase, Surfactant, and Temperature^a

oil phase ^b	surfactant	wt % surfactant ^c	45 °C	65 °C
CO ₂	PBO- <i>b</i> -PEO	0.5	7 ± 2	47 ± 3
CO ₂	PDMS- <i>g</i> -PEO	0.1	5 ± 1	41 ± 2
CO ₂	PFPE COO ⁻ NH ₄ ⁺	0.5	6 ± 2	43 ± 2
CO ₂	no surfactant	0		29 ± 4
<i>n</i> -octane	AOT	0.5	5 ± 2	33 ± 3
<i>n</i> -octane	no surfactant	0		29 ± 2

^a Reaction conditions: 2 M potassium bromide in the aqueous phase and 0.11 M benzyl chloride in the oil phase. Average product yield of benzyl bromide (of ≥ 2 experiments) after 5 h. 50/50 wt % water/oil phase. ^b Reactions with CO₂ were performed at 4000 psia and reactions with *n*-octane at atmospheric pressure. ^c wt % relative to the total weight of both water and oil phase.

Results

The synthesis of benzyl bromide was conducted with both anionic (PFPE COO⁻NH₄⁺) and nonionic (PBO-*b*-PEO and PDMS-*g*-PEO) surfactants in emulsions of water and CO₂. For comparison purposes the reaction was also performed with H₂O/*n*-octane emulsions stabilized with the anionic surfactant AOT. The amount of surfactant used to form the emulsions was 0.5 wt % except in the case of PDMS-*g*-PEO where it was only 0.1 wt %. For both solvent systems the reaction was also performed in the absence of any surfactant.

In the data presented, the concentration of potassium bromide in the H₂O phase was kept at 2 M while the concentration of benzyl chloride was 110 mM in the CO₂ phase. This gave a 15:1 molar ratio of salt:substrate, which leads to a pseudo-first-order reversible reaction.

In Table 1 the average product yield of benzyl bromide after 5 h at various reaction conditions is given. The effect of temperature was the same for all reaction systems. A lower temperature of 45 °C gave yields less than 10% while at 65 °C the yields increased to 30–47%. The highest yields were obtained in the emulsions, with a slightly larger value for the nonionic surfactant PBO-*b*-PEO (47%) as compared to the anionic surfactant PFPE COO⁻NH₄⁺ (43%). The PDMS-*g*-PEO emulsions gave a slightly lower yield of 41%. Without any added surfactant, the product yield of benzyl bromide was essentially the same for the suspensions in both CO₂ and *n*-octane (29%). This value is significantly smaller than that in the w/c emulsions containing surfactant. The difference is far greater than the experimental uncertainty, which was at most ±3% in the emulsion experiments. Adding AOT to the H₂O/*n*-octane suspension to form an emulsion gave only a slight increase in yield, 33% as compared to 29% without surfactant.

In Figure 1 data from a series of reactions performed at 65 °C with different surfactants and solvents are shown. In the case of the w/o emulsions the yields after 5 h with AOT or without any surfactant are within 10% (Table 1). The difference in the initial rates for these two cases appears to be larger than the difference in yields after 5 h. The highest initial rates were obtained with the PBO-*b*-PEO followed by the PFPE COO⁻NH₄⁺ emulsions. For PDMS-*g*-PEO, the initial rate was considerably lower as compared to PBO-*b*-PEO and PFPE COO⁻NH₄⁺, but at later times the yield became closer to the others.

At 45 °C all reaction systems with surfactant formed emulsions easily within 10 min and were stable for as long as the reaction process was monitored. At 65 °C the emulsions with PBO-*b*-PEO and PDMS-*g*-PEO were less stable and harder to form. It was then essential to form the emulsion at a lower temperature and increase the

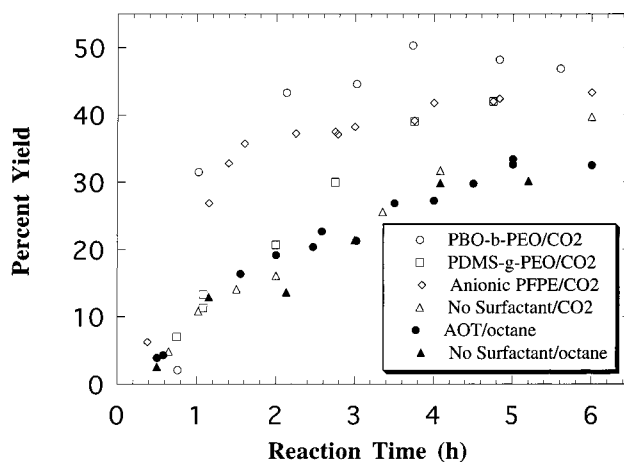


Figure 1. Product yield of benzyl bromide as a function of time with and without surfactant in emulsions formed with equal weights of water and carbon dioxide (65 °C at 4000 psia) and w/*n*-octane (1 atm) emulsions.

temperature to 65 °C while maintaining efficient stirring. In some cases, when the reaction was run for longer reaction times (> 3 h) the emulsions would break somewhat during the reaction process and the reaction cell would contain a lower emulsion phase and an upper CO₂ phase in a volume ratio of ca. 4:1. As the yield was relatively constant by this time, it did not have a significant effect on the product yields.

Discussion

A surfactant can influence a reaction in various ways, e.g., by emulsion or micellar catalysis.²¹ In micelles, microemulsion droplets, and emulsion droplets, the environment in the interfacial region is very different than that in the micelle core or the continuous phase. It is known that w/c microemulsions may be formed with PFPE COO⁻NH₄⁺.³ Therefore, microemulsion droplets will be present along with the larger emulsion droplets, a scenario that is well-known for water-in-oil emulsions.²² For PBO-*b*-PEO, we found that microemulsions are not formed based on the insolubility of the appropriate amounts of water in surfactant/CO₂ solutions.

For ionic surfactants, the highly charged interfacial region can catalyze reactions. Catalysis by surfactant headgroups, especially for reactions with a change in charge from the reactant state to the transition state, may be expected to be smaller in emulsions where the surfactant molecules are spaced farther apart than for microemulsions.¹³ The benzyl chloride reaction has been shown to be catalyzed by cationic micelles.²³ This effect has also been seen for other micellar reactions involving other anionic nucleophiles, where a cationic surfactant catalyzes the reaction while an anionic surfactant inhibits it.²⁴ Therefore, nonionic and anionic surfactants are not likely to catalyze the reaction, but they do increase the amount of surface area between water and CO₂. Because an emulsion droplet (0.5–10 μm) is typically on the order

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of 100–1000 times larger than a microemulsion droplet, the surface area/volume is 100–1000 times smaller. However, this surface area/volume ratio is still much larger than that in suspensions of water droplets in an oil or CO₂ without surfactant, where droplets are much larger.

The slightly lower yield for PFPE COO⁻NH₄⁺ as compared to PBO-*b*-PEO suggests that the reaction may be slightly inhibited by anionic headgroups at the interface. Here, the nucleophile in the aqueous phase is repelled from the interface by the negative charge on the surfactant headgroups. This negative charge will also destabilize the negatively charged transition state. However, a comparison of the yield with and without PFPE COO⁻NH₄⁺ indicates that this inhibiting effect is small compared to the advantage of the increased surface area. The lower yields obtained with PDMS-*g*-PEO, as compared to PBO-*b*-PEO and PFPE COO⁻NH₄⁺, is probably an effect of the lower surfactant concentration, 0.1 as compared to 0.5 wt %.

The synthesis of benzyl bromide has previously been performed by phase transfer catalysis (PTC) in CO₂.²⁵ Here, the headgroup of a cationic catalyst shuttles bromide and chloride ions between the organic and aqueous phases. This mechanism can be ruled out in our case as no cationic surfactant was used. Also, the concentration of surfactant used in the w/c or c/w emulsion experiments (0.3–9 mM) was much lower than that typically used in PTC.²⁶ To date, w/c microemulsions or emulsions have not been reported for cationic surfactants.

The reactions in H₂O/*n*-octane emulsions stabilized by AOT were performed at atmospheric pressure. Because pressures up to 4000 psia have little effect on emulsions in incompressible liquid solvents, it is unlikely that the lower yield for this reaction is due to the low pressure. Pressure can influence emulsions in liquid solvents if the emulsion is very near the phase inversion temperature,¹⁸ which is not the case here.

The nature of the water–CO₂ interface is likely very different than that of a water–alkane interface due to the lower γ for the former and the small size and low viscosity of CO₂. The higher yields for the w/c or c/w versus w/o emulsions are likely due to these factors. The very low viscosity for this interface and the high diffusion coefficients in the CO₂ phase may accelerate the reaction rate. This acceleration may be expected to be greatest for fast reactions approaching the diffusion controlled limit. Because benzyl bromide synthesis is relatively slow, the increase in yield from suspensions of water without surfactant to w/c or c/w emulsions was relatively modest. Recently, we have confirmed that emulsions produce much greater increases in reaction rates for faster reactions.²⁷ In the case of no surfactant, the yields of benzyl bromide in w/c and w/o mixtures were comparable, due to the considerably smaller surface area between the two phases. Only with the much greater surface area obtained in an emulsion will the difference between the two biphasic systems give a significant difference in yields.

The yields of benzyl bromide were far greater in w/c emulsions relative to w/c microemulsions.⁷ The main

reason for this difference is that the microemulsions were limited by the amount of salt that could be dissolved in the aqueous microemulsion droplets. The volume fraction of the dispersed water was below 1 wt % in the microemulsion compared to 50 wt % in the emulsion. The maximum W_0 (mol ratio of water to surfactant) for these microemulsions was less than 10 with high concentrations of salt, compared to 20 with pure water. Therefore, w/c emulsions are currently more suitable than w/c microemulsions for reactions requiring large amounts of a hydrophile. These results correlate with previously published data where synthesis of alkylphenyl ethers gave higher yields in two-phase emulsions¹³ as compared to single-phase o/w micelles,²⁴ due to the higher reactant solubility in the former.

The amount of benzyl alcohol formed, due to hydrolysis of benzyl chloride, was less than 4% under all reaction conditions. This low selectivity to benzyl alcohol illustrates that w/c or c/w emulsions may be used to shield substrates which are easily hydrolyzed from water. The amount of H₂O soluble in the CO₂ phase is only 4 mg/g of CO₂ at 65 °C and 4000 psia, not enough to lead to hydrolysis.

Conclusions

The use of a w/c or c/w emulsion for reactions between hydrophilic and hydrophobic compounds is a new environmentally friendly technique which gives higher yields as compared to a w/o emulsion for the reaction studied. The higher yields may be attributed to the lower interfacial tension and viscosity for a H₂O–CO₂ interface as compared to a H₂O–alkane interface, along with the higher diffusivity in the CO₂ phase. Also, no organic solvent or cosolvent is needed to form these emulsions. The emulsion is easily broken by decreasing the pressure to separate the water and CO₂ phases, facilitating product recovery and CO₂ recycle. Compared to presently available w/c microemulsions, much higher concentrations of hydrophilic substrates can be dissolved in w/c emulsions, with substantial increases in reaction yields.

The reaction between benzyl chloride and potassium bromide in w/c (or c/w) emulsions was studied for both anionic (PFPE COO⁻NH₄⁺) and nonionic (PBO-*b*-PEO and PDMS-*g*-PEO) surfactants. Higher yields (41–47%) were obtained in the emulsions as compared to the yields in w/c microemulsions (30%) and w/o emulsions (33%) stabilized by the anionic surfactant AOT. The type of surfactant headgroup had less effect on the reactions in emulsions as compared to microemulsions, indicating that the primary role of the surfactant was to increase the interfacial area. Without any added surfactant the yields in H₂O/CO₂ and H₂O/*n*-octane biphasic systems were comparable (29%) and lower as compared to the emulsion reactions, due to the much smaller surface area in the biphasic systems. Even larger increases in yields from the use of a w/c emulsion as reaction media may be expected for fast reactions approaching the diffusion controlled limit.

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