Organic Synthesis in Water/Carbon Dioxide Microemulsions

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Nucleophilic substitution reactions were performed in H_2O/CO_2 (w/c) microemulsions formed with an anionic perfluoropolyether ammonium carboxylate (PFPE $COO^-NH_4^+$) surfactant. These reactions between hydrophilic nucleophiles and hydrophobic substrates were accomplished in an environmentally benign microemulsion without requiring toxic organic solvents or phase transfer catalysts. For the synthesis of benzyl bromide from benzyl chloride and KBr, the yield was an order of magnitude higher in w/c microemulsions versus conventional water-in-oil (w/o) microemulsions. Benzoyl chloride and *p*-nitrophenyl chloroformate were hydrolyzed in w/c microemulsions with rate constants an order of magnitude faster than those in w/o microemulsions.

Introduction

When performing synthetic organic chemistry, one is often faced with the problem of reacting a hydrophobic compound with one that is hydrophilic, e.g., a salt. One approach is to add a cosolvent to mix water with an organic solvent. Although this approach makes the organic substrate accessible to the water soluble reagent, it also increases the contact of the substrate with water, promoting competitive hydrolytic pathways. Another possibility is to add a phase transfer catalyst (PTC), typically a quaternary ammonium compound. The catalyst forms a complex with the hydrophilic substrate in the aqueous phase and shuttles it into the organic phase, allowing the two substrates to react.[1] A disadvantage of phase transfer catalysis is that the organic solvent and PTC can be toxic. Recently this technique has been applied to the interface between a solid suspended salt and CO_2 as a replacement for an organic solvent.[2]

Another approach is to use a microemulsion, which is a thermodynamically stable and optically transparent microheterogeneous system.[3] Microemulsions, with droplet sizes in the range of 50−500 Å, are formed by adding an amphiphile to a system containing water and oil (usually a hydrocarbon). A cosolvent is often needed for formation of a microemulsion to achieve the proper balance of attractive and repulsive interactions on the hydrophobic and hydrophilic sides of the interface. The cosolvent reduces the interfacial tension between the droplets and the continuous phase.[4] Microemulsions are good solvents for both hydrophilic and hydrophobic reactants and have been utilized as media for catalytic[5] and enzymatic[6] reactions, for enhanced oil recovery,[7] and as a mobile phase in chromatographic solutions.[8]

In a microemulsion, high concentrations of both water-soluble and water-insoluble compounds can be dissolved simultaneously. Also, the surface area between water and oil can reach values as high as 10^5 m^2 per liter of microemulsion.[9] When both reactants are concentrated inside a microemulsion droplet, it functions as a nanoreactor, and the size of the droplet can have a significant influence on the reaction kinetics. In the case where one reactant is in the continuous phase and the second in the dispersed phase, the partitioning of the reactants in the interphase is of great importance. The reaction can take place inside the microemulsion droplet, at the surfactant interface, or in the continuous phase. Depending upon the charge of the surfactant headgroup, a reaction may either be catalyzed or inhibited. Recently, a phase transfer catalyst has been added to both microemulsions[10] and emulsions[11] to facilitate transfer across the interface; furthermore, high organic substrate concentrations were used.

Most studies of reactions in microemulsions have been performed with reactant concentrations below 0.1 M, which are somewhat low for conventional synthetic organic chemistry and especially for industrial applications. In a few cases, reactant concentrations above 1 M have been used.[4,10−12] In these cases, it was necessary to compensate for the influence of the reactants on the stability of the microemulsion by using higher surfactant concentrations.

Microemulsions can also be formed by using supercritical fluids as the nonaqueous phase, as reviewed elsewhere.[13] Supercritical fluids have liquid-like densities

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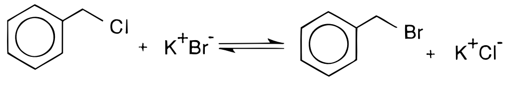
and gas-like diffusivities and viscosities.[14] The adjustable physical properties of supercritical fluids, for example, the density, have been utilized in areas such as chromatography and extraction,[15] synthesis,[16] and materials processing. Supercritical and near-critical alkanes, such as ethane and propane, have been used to form water/alkane microemulsions.[17] Recently, water-in-CO_2 (w/c) microemulsions were formed with a hybrid hydrocarbon−fluorocarbon surfactant[18] and PFPE $COO^-NH_4^+$.[19] For the latter microemulsion, water pools with properties approaching bulk water were characterized with FTIR, fluorescence, UV−vis, and electron paramagnetic resonance spectroscopy and by neutron scattering.[19,20] These microemulsions may be used to perform interfacial inorganic reactions, e.g., between CO_2-soluble gases, such as H_2S and SO_2, and water-soluble inorganic salts.[21]

Carbon dioxide is an attractive alternative to organic solvents as it is environmentally benign, essentially nontoxic, inexpensive, nonflammable, and has relatively low critical conditions ($P_c = 73.8$ bar, $T_c = 31$ °C). Its limited use in organic synthesis has been due to its weak van der Waals forces, as characterized by its low polarizability per volume, making it unable to solvate many polar and ionic nonvolatile materials. Solubilities can be increased by adding small amounts of cosolvent (e.g., methanol), although a majority of the hydrophilic compounds such as proteins are still very insoluble.

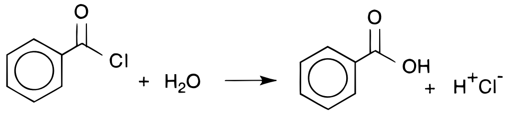
The possibility of achieving high solubilities of both hydrophilic and hydrophobic compounds in w/c microemulsions offers a new opportunity for synthetic organic chemistry where no toxic organic solvents or catalysts are needed. Another advantage of these w/c microemulsions is that only a modest amount of surfactant (<1.5 wt %) is needed to achieve a sufficiently low interfacial tension to form the microemulsion. The interfacial tension, γ, between H_2O and CO_2 is on the order of 18 mNm^{-1} at pressures above 70 bar,[22] much lower than that between H_2O and alkanes (30−50 mNm^{-1}).[9] The lower γ may facilitate reaction between organic substrates and hydrophilic reactants at the interface. This lower γ reflects the fact that CO_2 is more miscible with water than are alkanes, because of its acidity and quadrupole moment. To achieve low values of γ required to form microemulsions, less surfactant may be required for CO_2 than for alkane continuous phases, since γ without surfactant is only 18 mNm^{-1}.

In this paper, we report the first attempt to perform a synthetic organic reaction in a w/c microemulsion. As a simple model we chose to study the reaction between benzyl chloride **1** and potassium bromide to form benzyl bromide **2**. This reaction between a nonaqueous compound soluble in CO_2 and a CO_2-insoluble salt may be expected to take place at or near the surfactant interface. This reaction has previously been performed in both W/O and O/W microemulsions,[23] with triphase catalysis[24] and with PTC in supercritical CO_2.[2] Our results will be compared to these studies.



1 **2**

Carboxylic ester hydrolyses, catalyzed by nucleophiles and enzymes, are commonly occurring reactions in biological systems. Therefore the investigation of ester hydrolyses in w/c microemulsions is of obvious importance. To further compare the use of supercritical carbon dioxide to hydrocarbons as a continuous phase in microemulsions for synthetic organic chemistry, we chose to study the hydrolysis of benzoyl chloride **3** and *p*-nitrophenyl chloroformate **5**. Both of these substrates are water-insoluble and have been studied extensively in microemulsions.[25]



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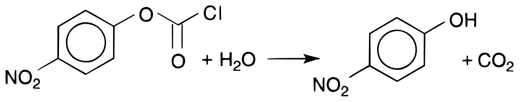

5 **6**

The addition of reactants to the microemulsion can have a large effect on the phase behavior of the system, especially for the high concentrations of substrates desired for synthetic purposes. Phase behavior studies were therefore conducted to ensure that all reactions were performed in a single homogeneous phase.

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, benzoyl chloride, *p*-nitrophenyl chloroformate, anisole, naphthalene, and *n*-octane were all obtained from Aldrich and used without further purification. Instrument grade carbon dioxide (Praxair Inc.) was passed through an oxygen

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trap (Oxyclear model no. RGP-31-300, Labclear, Oakland, CA) before entering an ISCO syringe pump (model 260D) which was used to load the reaction cell. Nanopure II water (Barnstead, Dubuque, IA) was used in all experiments. The PFPE $COO^-NH_4^+$ was a gift from Alba Chittofrati, synthesized according to published procedures.[26] For the benzyl bromide synthesis the molecular weight of PFPE $COO^-NH_4^+$ was 740 g/mol, and for the hydrolysis it was 940 g/mol.

Product mixtures were analyzed by GC (Hewlett-Packard model 5890A) equipped with an fused silica precolumn (i.d. = 0.53 mm, 0.5 m, methylated, Supelco) followed by a SPB-5 column (i.d. = 0.53 mm, 30 m, Supelco). Cool on-column injection and FID detection were used. Appropriate response factors relative to an internal standard (anisole or naphthalene) were determined for each substance analyzed. Nitrogen was used as carrier gas at 30 mL/min, and the following temperature gradients were used for analyzing the synthesis of (A) benzyl bromide, 80 °C, 0.5 min; 15 °C/min; (B) benzoic acid, 75 °C, 0.5 min; 10 °C/min; and (C) *p*-nitrophenol, 80 °C, 0.5 min; 20 °C/min.

High-Pressure Apparatus. The reactions were performed in a variable-volume view cell described previously.[27] The cylindrical stainless steel cell (2 in. o.d. × $^{11}/_{16}$ in. i.d., 35.2 mL total volume) was equipped with a sapphire window (1 in. diameter by $^{3}/_{8}$ in. thick). A piston inside the cell allowed the pressure and temperature to be varied independently. The reaction mixture was stirred by the use of a Teflon-coated magnetic stir bar. A gear pump (1750 rpm, Baldor Electric Co., Ft. Smith, AR) was used to constantly recirculate the solution through a 6-port 2-position valve (C6W, Valco Instruments Co., Inc., Houston, TX) equipped with a 100 μL sample loop, allowing samples to be taken throughout the reaction process. At the desired sampling time the valve was switched and the sample was trapped in ca. 500 μL of liquid solvent for analysis by GC.

The surfactant, water, KBr (when used), internal standard, and a stir bar were loaded into the reaction cell, which was then filled with a known volume of CO_2. The cell assembly was placed in a polycarbonate water bath, which also served as a safety shield, and temperatures were controlled to ±0.1 °C. After the microemulsion was formed at the desired temperature and pressure by stirring the cell contents, the hydrophobic reactant was injected into the cell from the sample loop, starting the reaction.

Low-Pressure Experiments. The experiments using the AOT surfactant in H_2O/*n*-octane were performed in a 100 mL round-bottomed flask at atmospheric pressure. AOT, water, *n*-octane, internal standard, and salt was added together with a stir bar into the flask which was then heated in a water bath (as described above). After the microemulsion formed, the hydrophobic reactant was added and the reaction was followed by analyzing aliquots of the reaction mixture by GC.

Phase Behavior Studies. The same high-pressure experimental setup was used with the exception that the gear pump and the Valco valve were disconnected from the apparatus and two ports were plugged. The required amount of PFPE $COO^-NH_4^+$ needed to obtain a 1.4 wt % solution in CO_2 was loaded into the variable volume view cell together with the desired amount of water. After the cell was closed, carbon dioxide was added into the cell and also used to pressurize the cell from the back of the piston. The solution was stirred for at least 1 h at the desired temperature and at a pressure to ensure a homogeneous microemulsion. The stirring was stopped, and the pressure was gradually lowered until a cloudy solution was seen through the sapphire window. This pressure was defined as the cloud point pressure and was measured at least three consecutive times. The mean value at each temperature was reported. The typical uncertainty was <10 psia.

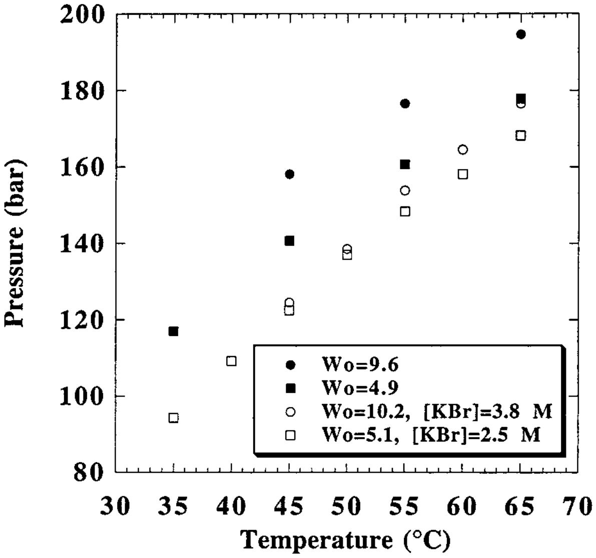

Figure 1. Cloud point pressure versus temperature for PFPE $COO^-NH_4^+$ w/c microemulsions with varying W_o and salt concentrations. The two curves without added salt are taken from Heitz; et al. *J. Phys. Chem.* **1997**, *101*, 6707.

Results

Phase Behavior Study. The phase behavior of the PFPE $COO^-NH_4^+$ w/c microemulsion was measured to study the effect of added salt on the cloud point pressure. The goal was to determine the maximum amount of salt that could be dissolved in the aqueous micellar phase at a certain temperature and pressure while still forming a homogeneous microemulsion. The results are shown in Figure 1, which also contains previously published data for this system where no salt was added.[19] The size of the water pool in the aqueous core is proportional to the W_o value, the molar ratio of water to surfactant. At a given temperature and pressure, a certain amount of water is soluble in the CO_2 phase.[28] This amount was subtracted from the total amount of water added to the cell, to determine a corrected W_o. At a given temperature and W_o, the addition of salt lowers the cloud point pressure. The same behavior was observed for the propane/AOT/CO_2 system. For this system, it has been demonstrated theoretically and experimentally that the maximum W_o where a one-phase microemulsion is stable is governed by micelle−micelle interactions.[29] These interactions cause water and surfactant to precipitate at a W_o above this maximum. Apparently, the presence of salt weakens these interactions leading to a larger W_o at a given pressure. At a given W_o and pressure, a minimum temperature is required to form a one-phase microemulsion. Below this minimum temperature, a two-phase system is observed consisting an upper w/o microemulsion phase and a lower aqueous phase.

Synthesis of Benzyl Bromide in Microemulsions. The reaction of KBr and benzyl chloride in w/c microemulsions was studied with the surfactant PFPE-$COO^-NH_4^+$. The effect of W_o, substrate concentration,

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Table 1. Reaction of Benzyl Chloride and KBr in PFPE $COO^-NH_4^+$ w/c Microemulsions[a]

	W_o	[KBr] (M)[b]	[BnCl] (mM)[c]	mol KBr/ mol BnCl	yield (%)
1	4.6	4.7	1.9	3.5	6 ± 2
2	9.7	1.2	2.2	1.4	9 ± 3
3	9.7	4.1	1.1	9.7	17 ± 2
4	9.7	4.1	6.4	1.7	30 ± 3
5	9.7	4.1	10	1.0	28 ± 3

[a] Reaction conditions: 65 °C, 276 bar, 16 h, 1.4 wt % surfactant. The product mixtures were analyzed by GC. [b] Based on the total volume of water. [c] Based on the volume of CO_2.

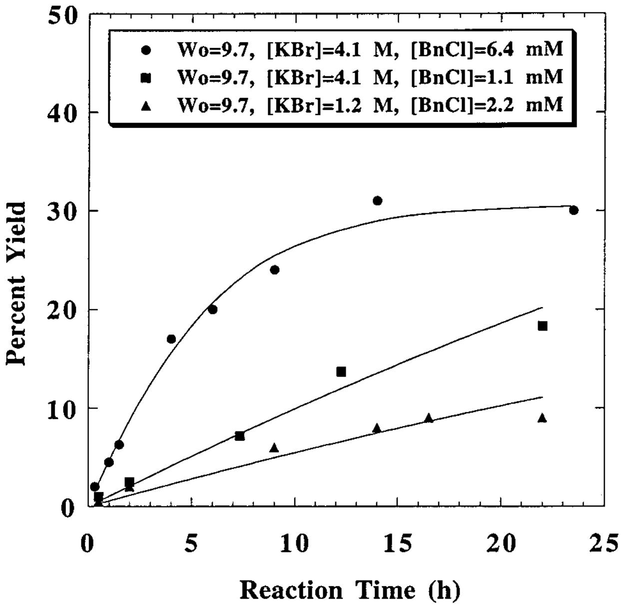

Figure 2. Yield for the reaction of benzyl chloride and KBr in PFPE $COO^-NH_4^+$ w/c microemulsions at 65 °C and 276 bar. The lines are fits of the data, and the constants are given in Table 2.

temperature, and pressure on the yield of benzyl bromide was investigated as shown in Table 1. These reactions were all run at 65 °C and 276 bar for 16 h with 1.4 wt % (16 mM) surfactant. From run 1 vs run 3−5**,** it can be concluded that lowering the W_o decreases the product yield. Runs 3−4 show that at constant W_o and [KBr] an increase in [BnCl] increases the yield. After that adding more BnCl (run 5**)** does not increase the yield further. The [BnCl] was not increased past 10 mM, where the molar ratio of KBr/BnCl was unity.

To elucidate the factors affecting the rates of the nucleophilic substitution, reactions in water-in-CO_2 microemulsions, runs 2−4, were fit to reversible, second-order kinetics of the form

$$-\frac{d[BnCl]}{dt} = k_f[BnCl][Br^-] - k_r[BnBr][Cl^-]$$

where k_f and k_r are forward and reverse rate constants and all concentrations are in terms of total volume. It was assumed that the value of the equilibrium constant K ($= k_f/k_r$) was equal in all experiments. Figure 2 shows the fits of the kinetic model, and Table 2 contains the regressed equilibrium and forward rate constants, along with the calculated equilibrium conversions. The rate constants for runs **2** and **4** were in good agreement; the reason for the lower value for run 3 was not obvious. The mechanism of the interfacial reaction may have been somewhat different for the lower [BnCl] and the high ratio of KBr to BnCl. Increasing the [KBr] from 1.2 to 4.1 M had a fairly large effect on the product yield (compare runs 2 to 3) as expected. The maximum [KBr] that could be achieved at a $W_o \approx 10$ was 4.1 M; adding more salt split the homogeneous microemulsion into a two-phase system.

Table 2. Reversible, Second-Order Kinetics for the Reaction of Benzyl Chloride + KBr

	K	k_f (M^{-1} h^{-1})	equilibrium convn (%)
2	0.097	3.8	28
3	0.097	0.99	60
4	0.097	4.4	31

Using otherwise the same reaction conditions as in runs 1−5, these experiments were also conducted at 45 °C which in all cases decreased the product yields to <2%. Increasing the surfactant concentration to 3 wt % (30 mM) at both 45 and 65 °C did not, on the other hand, have any significant effect on the yields. The effect of pressure was only significant if it was lowered below the cloud point pressure where a two-phase system and lower yields were observed. No traces of benzyl hydroxide detectable by GC were observed in any of these reactions, suggesting that the reaction took place in a nonaqueous environment, e.g., at the micellar interface.

To place these results in perspective, experiments were also performed with the commonly used anionic surfactant system AOT/H_2O/*n*-octane. For the same surfactant concentration, W_o, and reactant concentrations as in run 4, experiments were performed at atmospheric pressure at both 45 and 65 °C. This allowed the use of supercritical CO_2 as a continuous phase to be compared to the more commonly used hydrocarbon solvents. With AOT/H_2O/*n*-octane microemulsions, less than 2% product yield was obtained in 24 h at both 45 and 65 °C.

Hydrolysis Reactions. The hydrolysis of benzoyl chloride **3** and *p*-nitrophenyl chloroformate **4** in PFPE $COO^-NH_4^+$ w/c and AOT/H_2O/*n*-octane microemulsions were performed to further study the use of supercritical CO_2 as a nonaqueous phase for synthetic chemistry. Both of these substrates are water-insoluble. In these experiments, the concentration of the hydrophilic reactant, water, was much higher than the KBr concentration in the benzyl bromide synthesis. All reactions in CO_2 were performed at 35 °C and 276 bar. A substrate concentration of 0.05 M was used in order to achieve a great excess of water to ensure pseudo- first-order kinetics. At a W_o of 10, the yield was 45% for the hydrolysis of benzoyl chloride in 25 h and for that of *p*-nitrophenyl chloroformate in 9 h.

The observed pseudo-first-order rate constant k_{obs}

$$k_{obs} = k[H_2O]$$

was measured for the hydrolysis reactions at W_o values of 5 and 10 (Table 3). At a W_o of 5 the observed rate constant for hydrolysis of *p*-nitrophenyl chloroformate is slightly higher than that for benzoyl chloride in the respective microemulsion systems. The reverse was observed at the higher W_o value of 10, with slightly higher reaction rates for benzoyl chloride in both cases. In all cases though, the reaction rates were an order of magnitude lower for the w/octane as compared to the w/c microemulsions.

Table 3. Hydrolysis Reactions in Microemulsions[a]

substrate	microemulsion	$W_o = 5$		$W_o = 10$	
		k_{obs} (s^{-1})	R^b	k_{obs} (s^{-1})	R^b
benzoyl chloride	H_2O/PFPE/CO_2	1.7×10^{-6}	0.99	6.4×10^{-5}	0.98
	H_2O/AOT/*n*-octane	3.0×10^{-7}	0.94	3.4×10^{-6}	0.92
p-nitrophenyl chloroformate	H_2O/PFPE/CO_2	2.9×10^{-6}	0.97	1.6×10^{-5}	0.94
	H_2O/AOT/*n*-octane	5.9×10^{-7}	0.99	7.6×10^{-7}	0.99

[a] Conditions: 35 °C, 276 bar in the case of CO_2 and atmospheric pressure for *n*-octane, [substrate] = 0.05 M. The product mixtures were analyzed by GC. [b] Correlation coefficient for the least-squares fit of ln c/c_o vs time.

Discussion

KBr is insoluble in CO_2, and benzyl chloride is insoluble in water. As a consequence, the reaction must either occur at the interphase or some other mechanism must be present to transfer one reactant into the other phase. No benzyl hydroxide, detectable by GC, was observed in any of the reactions, also suggesting that the reaction takes place in a nonaqueous environment, e.g., at the micellar interface.[23,24a]

The limiting factor in the synthesis of benzyl bromide was the amount of salt that could be dissolved in the aqueous micellar core. Without any added salt the maximum W_o value that has been reported for PFPE $COO^-NH_4^+$ w/c microemulsions is 20.[18] With high concentrations of added salt (up to 4 M), it was not possible to obtain a W_o above 10 at temperatures of 65 °C. Higher salt concentrations could be obtained at lower temperatures although the decrease in rate due to decreased temperature is far greater than the increase obtained by higher reactant concentrations.

In previous studies of nucleophilic substitution reactions in microemulsions, it has been shown that cationic surfactants can increase the reaction rate as compared to nonionic and especially anionic surfactants. In the latter case inhibition of the reaction rate has even been reported. These results are explained by the fact that a negatively charged transition state is stabilized by a cationic surfactant headgroup, thereby attracting it to the interphase where the reaction takes place. To date cationic surfactants have not been developed which can form w/c microemulsions. However, our product yields with the anionic surfactant PFPE $COO^-NH_4^+$ are comparable to or even greater than those reported by Martin et al.[23] in a w/o microemulsion stabilized by a cationic surfactant at comparable reaction conditions. Furthermore, in their study, the surfactant concentration was 6 times higher and butanol was needed as a cosolvent.

Higher yields for this reaction have been reported in o/w microemulsions,[23] although in this case the surfactant concentration was quite high (37 wt %). The byproducts benzyl hydroxide and benzyl butyl ether were also observed. Higher yields can also be obtained by adding a catalyst as in traditional PTC or triphase catalysis.[24] Dillow et al. added a PTC catalyst to supercritical CO_2,[2] with a small amount of acetone as a cosolvent to solubilize the catalyst. The larger KBr to benzyl chloride ratio compared with that in the pesent study led to a higher equilibrium conversion.

An advantage of the w/c microemulsions for phase transfer reactions is that organic solvents and catalysts, both which may be toxic, are not needed. Only small amounts of PFPE $COO^-NH_4^+$, an environmentally benign surfactant, are required. After reaction, the solvent strength of CO_2 may be tuned to separate reactants and product, and solvent recovery and recycle are particularly efficient. A disadvantage however is that high pressures are needed.

The structure of the interfacial water in reverse micelles has been shown to change with increasing W_o.[30] In the case of a surfactant such as PFPE $COO^-NH_4^+$, added water initially hydrates the anionic headgroups, first binding to the anionic side of the ion pair and thereafter hydrating the cation.[25b] Further added water is incorporated into the micellar core, and as W_o increases the micelles swells. Water in the periphery is more structured and has different physical properties, e.g., lower polarity, as compared to bulk water.[31] Only in large water droplets do the physical properties resemble those of bulk water.

The effect of varying physical properties of the interfacial water was observed in the change of hydrolysis rates for benzoyl chloride and *p*-nitrophenyl chloroformate in the microemulsions. The fact that the hydrolysis rate of benzoyl chloride was greater at a W_o of 10 as compared to the rate of *p*-nitrophenyl chloroformate hydrolysis and that the reverse is true at a W_o of 5 is consistent with earlier published results[25b] and has been explained by the difference in mechanism between the two substrates.[25] For both compounds the mechanism involves nucleophilic addition of water at the carbonyl carbon, giving a tetrahedral intermediate, and cleavage of the C−Cl bond. In the case of benzoyl chloride the C−Cl bond breaking has progressed further in the transition state, as compared to *p*-nitrophenyl chloroformate, due to conjugative electron release by the aryl group which assists in the bond breaking. Therefore the reaction is less sensitive to the nucleophilicity of water and is instead favored by higher water polarity (which increases with increasing W_o) which stabilizes the cationic acylium ion and also the nucleofuge. The aryloxy group in *p*-nitrophenyl chloroformate assists nucleophilic attack, due to its inductive electron attraction, and the reaction is more sensitive to the nucleophilicity of the water molecules in the micelles. A reduction in the droplet size (W_o) leads to concentration of the anionic charge of the surfactant headgroups and stronger hydrogen bonding between the surfactant and water, thereby enhancing the nucleophilicity of the interfacial water.[25b] For *p*-nitrophenyl chloroformate hydrolysis, only a slight decrease in rate was observed as W_o was decreased from 10 to 5, much less than that for the hydrolysis of benzoyl chloride. Thus, the different effects of W_o on these two reactions is consistent with the expected changes in nucleophilicity and polarity of water.

For both hydrolysis reactions the rates were an order of magnitude higher for the w/c system as compared to

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(31) (a) Mukerjee, P. In *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 1, p 153. (b) Cordes, E. H.; Gitler, C. *Prog. Bioorg. Chem.* **1973**, *2*, 1.

H_2O/AOT/*n*-octane under otherwise similar reaction conditions. In earlier studies of the latter system,[25b] it was shown that addition of certain additives (such as sodium perchlorate and 1,3-dimethyl urea) increased the hydrolyses rates of these reactions by decreasing the viscosity at the micellar interface. An overall lowering of the microviscosity (ca. 30% less than bulk water) within the PFPE $COO^-NH_4^+$ microemulsion core has been suggested due to presence of CO_2.[20] This reduction in microviscosity likely contributes to the higher hydrolysis rates relative to w/o microemulsions.

Performing hydrolyses reactions in w/c microemulsions could be advantageous in cases where a water-insoluble substrate is involved. High concentrations of certain organic compounds can be dissolved in carbon dioxide, and the large surface area and low microviscosity of these microemulsions facilitates the interfacial reaction.

Conclusions

We have demonstrated that organic synthesis between hydrophilic nucleophiles (Br^- and water itself) and CO_2-soluble reactants can be performed in a w/c microemulsion containing small (<1.5 wt %) amounts of an environmentally benign surfactant, PFPE $COO^-NH_4^+$. No organic solvent is needed. Reaction yields and rate constants were larger by an order of magnitude in w/c microemulsions versus H_2O/AOT/*n*-octane microemulsions under similar conditions (except pressure). The enhanced reaction rates are likely due to the considerably lower microviscosity in w/c as compared to w/o microemulsions. The use of a tunable supercritical fluid offers the possibility of fractionation of products and may facilitate recovery and recycle of surfactant and CO_2. In the future, it would be desirable to find other microemulsion systems that could dissolve even larger amounts of water in CO_2.

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