# ORGANIC REACTIONS AND NANOPARTICLE PREPARATION IN $CO_2$ INDUCED WATER/P104/*P*-XYLENE/ MICROEMULSIONS

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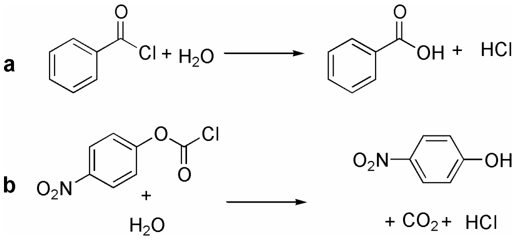
**Abstract:** Nanometer-sized gold particles are synthesized by the reduction of $HAuCl_4$ with $KBH_4$ in the $CO_2$ induced microemulsion of $(EO)_{27}(PO)_{61}(EO)_{27}$ (P104)/*p*-xylene/$CO_2$/$H_2O$. The recovery of the gold particles from the microemulsion can be easily accomplished by venting of $CO_2$, while the surfactant remains in the organic phase. The effect of the molar ratio of the reductant to $HAuCl_4$, the concentration of the reactants, and the $W_0$ (the molar ratio of water to EO segments) in the reverse micelles on the size of the gold particles is studied. The reaction of hydrolysis of benzoyl chloride (BzCl) and *p*-nitrophenyl chloroformate (NPhCl) has also been carried out in the microemulsion. The results show that the observed rate constant $k_{obs}$ of both substrates increase significantly with $W_0$, and $W_0$ has a larger influence on the hydrolysis of BzCl. The different extents of the influence of $W_0$ on the two reactions can be ascribed to the different reaction mechanisms and the expected changes in nucleophilicity and polarity of water in the reverse micelles.

## Introduction

Compressed $CO_2$ is quite soluble in a number of organic solvents and expands them largely. With the $CO_2$-expanded solvent medium, it is possible to achieve an optimum condition for some processes. Sometimes the $CO_2$-expanded solvent may excel either neat solvents or supercritical $CO_2$ [1]. Compared with the liquid solvent mixtures, the easily and completely separation of $CO_2$ from the liquid solvent after depressurizing is also advantageous.

Recently, we published a short communication to report a novel finding[2]. Compressed $CO_2$ could induce the formation of reverse micelles of block $(EO)_{27}(PO)_{61}(EO)_{27}$ (P104) in *p*-xylene. The copolymer could not form reverse micelles in the solvent at 40 °C. Using compressed $CO_2$ to tune the solvent properties, the reverse micelles were formed. The $CO_2$-induced reverse micelles could solubilize polar and ionic chemicals like methyl orange and cobalt chloride. The unique advantage of this kind of reverse micelles was that the formation and breaking of the reverse micelles could be repeated easily by controlling pressure. We are very interested in the applications of this kind of microemulsions. In this work, we study the hydrolysis of benzoyl chloride (BzCl) (Scheme 1, a) and *p*-nitrophenyl chloroformate (NPhCl) (Scheme 1, b), and explore the possibility to prepare the gold nanoparticles in the $CO_2$-induced microemulsion. The results indicate that the microemulsion can be used to carry out the reactions and to prepare nanoparticles with potential advantages.

These studies in turn give some information of the properties of the reverse micellar solution.



**Scheme I. hydrolysis reaction**

## Experimental Section

***Materials*** P104 was provided by BASF Corporation with a composition of $(EO)_{27}(PO)_{61}(EO)_{27}$. BzCl, p-xylene, hydrogen tetrachloroaurate ($HAuCl_4$) and potassium borohydride ($KBH_4$) were AR Grade, and were supplied by Beijing Chemical Reagent Factory. NPhCl, ≥ 97% purity, was obtained from Aldrich and used as received. $CO_2$ (99.995% purity) was supplied by Beijing Analytical Instrument Factory. Double distilled water was used throughout the experiment.

***Apparatus and procedures to study the phase behavior*** The apparatus and procedures for studying the phase behaviors of $KBH_4/H_2O/P104/p$-xylene/$CO_2$ and $HAuCl_4/H_2O/P104/$ $p$-xylene/$CO_2$ microemulsions were the same as that used to investigate the phase behavior of $P104/H_2O/p$-xylene/$CO_2$ system used previously[2].

***The apparatus and procedures to study the hydrolysis reaction*** The apparatus to conduct the hydrolysis reaction was similar to that for determining the phase behavior described above. The main difference was that there was a six-port valve equipped with a sample loop, which was used to charge the hydrophobic reactants.

In a typical reaction, the air in the high-pressure view cell was replaced by $CO_2$. 5 g solution of P104 in *p*-xylene (15 wt%) and known amount of water were loaded into the reaction cell. Then the cell was placed into the constant temperature water bath of 40.0 ºC. After thermal equilibrium had been reached, the magnetic stirrer was started and $CO_2$ was compressed into the cell to the desired pressure. After the addition of $CO_2$, the hazy and milky solution became homogeneous and transparent which indicated the formation of the microemulsion. The hydrophobic reactant (BzCl or NPhCl dissolved in *p*-xylene) was injected into the high-pressure view cell through the sample loop of the six-port valve and the reaction started. After stirred for 10 hours, the reaction mixture was subjected to column chromatography to remove the surfactant P104. The products were then analyzed by HPLC (DuPont instrument, model 8800).

***The apparatus and procedures to synthesize and recover Au nanoparticles*** The apparatus for synthesis of the gold nanoparticles in microemulsion consisted mainly of a constant temperature water bath, a high-pressure syringe pump (DB-80), a the pressure gauge, a the magnetic stirrer, and the high-pressure cell. The key function of the cell was that it could mix the two solutions under pressure if necessary. It consisted mainly of a stainless steel body, a stainless steel baffle with Teflon seal on the edge, and a handle. The baffle could divide the cell into two chambers. The solutions in the two chambers could be mixed by adjusting the position of the handle under pressure.

In the experiment, the aqueous solutions of $HAuCl_4$ and $KBH_4$ of desired concentrations were freshly prepared separately. The cell was flushed with $CO_2$ to remove the air. Chamber A and Chamber B of the cell were charged with the solution of P104 in *p*-xylene. Desired amounts of $HAuCl_4$ and $KBH_4$ aqueous solutions were loaded into Chamber A and Chamber B, respectively. The cell was placed in the constant temperature water bath. After thermal equilibrium had been reached, $CO_2$ was compressed into the cell to the desired pressure and the stirrers in the two chambers were started to accelerate the formation microemulsions. The two micellar solutions containing $HAuCl_4$ and $KBH_4$ respectively were mixed by turning the baffle using the handle. Then gold nanoparticles were synthesized by reducing $HAuCl_4$ with $KBH_4$ in the reverse micelles. After the reaction $CO_2$ was slowly vented, which required about half an hour, and the gold nanoparticles were collected as precipitate because the reverse micelles were breaking after releasing $CO_2$. The organic solution was decanted and the precipitated gold particles are collected and washed with water. The size and shape of the obtained gold particles were determined by transmission electron microscopy (TEM) with a HITACHI H-600A electron microscope. The maximum resolution of the microscope is 0.5 nm. Particles were sonicated for 1 minute in ethanol and then directly deposited on the copper grid before the measurement.

***Apparatus and procedures for the UV study*** UV-Vis spectroscopy was used to monitor the synthesis of gold nanoparticles in the microemulsion. The UV-Vis apparatus was similar to those reported previously [3]. In the experiment, UV sample cell was connected with the two-chamber cell (see Figure 1, the connecting tube and the valve are not shown in the figure). The air in the UV sample cell was removed by a vacuum pump. The temperature of the cell was maintained at $40^{o}C$. Then the microemulsion with gold nanoparticles synthesized was transferred into the UV sample cell at constant temperature and pressure. The UV spectrum of the solution was then recorded every 10 minutes until it was unchanged.

## Results and discussion

***The phase behavior of system with and without $HAuCl_4$ and $KBH_4$*** The gold nanoparticles can be synthesized in the water core of microemulsions by the reduction of $HAuCl_4$ with $KBH_4$ [4]. We have studied the phase behavior of P104/*p*-xylene/$CO_2$/$H_2O$ microemulsion [2]. The results indicate that at 40 °C and ambient pressure of $CO_2$, the P104/*p*-xylene/$CO_2$ cannot solubilize water. As the pressure of $CO_2$ increases to a certain value, the water solubilization capability of P104/*p*-xylene/$CO_2$ solution increases abruptly. This indicates the formation of the reverse micelles. Addition of inorganic salt may affect the phase behavior of the microemulsion. Therefore, in this work we first investigate the phase behavior in the presence of $HAuCl_4$ and $KBH_4$, and the results illustrated that the salts did not affect the phase behavior considerably. In all the following sections, the results are obtained at 40.0 °C and the concentration of the polymer in the solution is 15 wt% (based on *p*-xylene).

***UV-Vis spectroscopy of the gold nanoparticles*** Colloidal dispersions of gold exhibit absorption bands in the UV-Vis range, which is due to the resonant excitation of surface plasmons. Thereby the gold nanoparticles stabilized in the reverse micelles can be analyzed in situ by the UV-Vis spectra. It is well known that the plasmon absorption peak at 525 nm is characteristic of gold particles larger than ~3 nm. This peak is red-shifted and is substantially broadened upon particle aggregation[4]. In this work, the spectrum of a ruby-colored solution of gold nanoparticles in P104/*p*-xylene/$CO_2$ microemulsion system shows an absorption peak at 525 nm (Figure 1).

***The recovery of the nanoparticles*** In this work, the reverse micelle formation is induced by compressed $CO_2$. The breaking of the reverse micelles can be accomplished simply by venting of $CO_2$. Therefore, solubilized Au nanoparticles in the reverse micelles can be precipitated after releasing the $CO_2$. Our experiment shows that the upper organic phase has no UV absorbance band of Au after $CO_2$ is released, which is an indication of the precipitation of the gold particles. The reversibility of reverse micelle system is the unique feature, and it is advantageous to recover the nanoparticles synthesized in the reverse micelles.

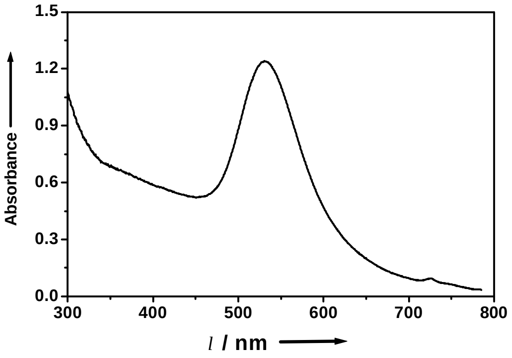
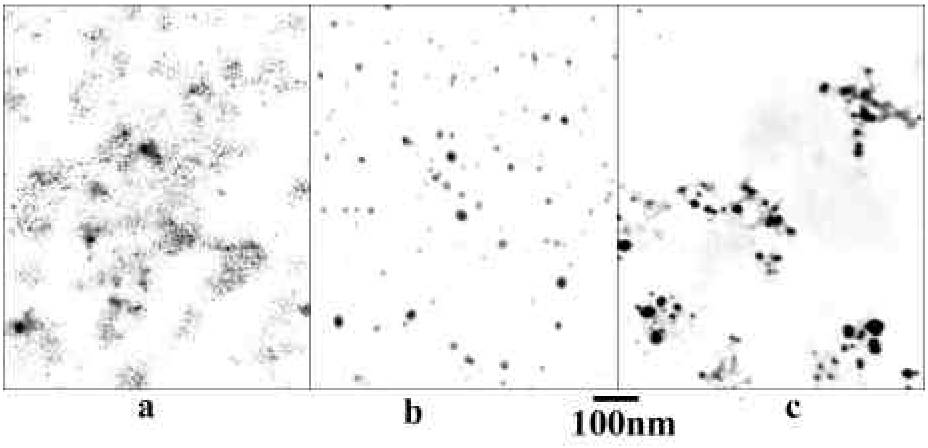


**Figure 1.** The UV-Vis spectrum of gold nanoparticles in P104/*p*-xylene/$CO_2$/$H_2O$.
$P = 5.75$ MPa, $W_0 = 2.9$, $[KBH_4] = [HAuCl_4] = 0.05 \text{mol l}^{-1}$

***The effect of operation condition on the size and size distribution*** Figure 2 illustrates the TEM photographs of gold nanoparticles synthesized in the microemulsion of P104/*p*-xylene/$CO_2$/$H_2O$ with different $W_0$. The diameter of the Au particle increases with increasing $W_0$. As the $W_0$ increases from 0.9 to 2.5, Au particle size increases from 6 to 30 nm. This may be ascribed mainly to the fact that the average number of reactant ions per droplet increase with increasing $W_0$.



a b c

**Figure 2.** TEM photographs of gold particles synthesized in P104/*p*-xylene/$CO_2$/$H_2O$

microemulsion with different $W_0$. a, $W_0$=0.9; b, $W_0$=1.5; c, $W_0$=2.5. The concentration of $KBH_4$ and $HAuCl_4$ are both 0.05 mol $l^{-1}$ in aqueous solution.

***Hydrolysis reactions*** The hydrolysis of BzCl and NPhCl (Scheme I) is performed in the P104/$H_2O$/*p*-xylene/$CO_2$ microemulsions. Both of these substrates are water-insoluble and known to be sensitive to the physical properties of the reaction medium[5]. The water is largely excessive to the substrate. So the hydrolysis can be treated with pseudo first-order kinetics. The observed pseudo first-order rate constants $k_{obs} = k[H_2O]$ determined for the hydrolysis reactions at different $W_0$ values are shown Figure 3.

The data in Figure 3 indicate that $k_{obs}$ increases with the increase of $W_0$ for both substrates. For example, the $k_{obs}$ at $W_0$ = 3.08 is almost ten times faster than that at $W_0$ = 1.03 for the hydrolysis of BzCl. It can also be seen from Figure 3 that the effect of $W_0$ on the rate constant of NPhCl is smaller than that of BzCl. The $k_{obs}$ of NPhCl hydrolysis is larger than that of BzCl at $W_0$ < 2.2, and becomes smaller at $W_0$ > 2.2. This is consistent with the earlier published results by other authors[6], who conducted the reactions in other microemulsions. This can been explained by the difference in mechanism of the two substrates.

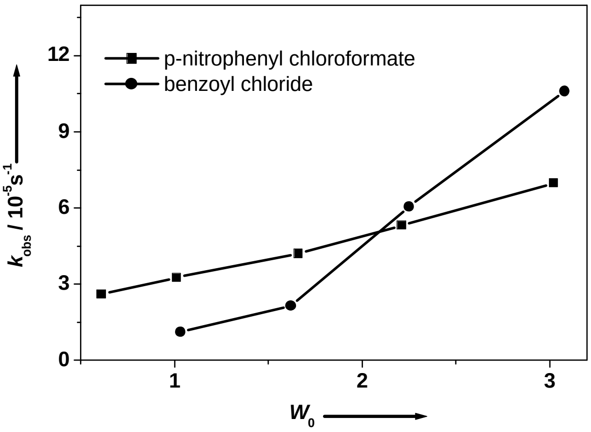


**Figure 3.** The variety of $k_{obs}$ with $W_0$

Both substrates are poorly soluble in water. Therefore, they preferentially solubilized in the hydrophobic phase (*p*-xylene/$CO_2$) and interphase of the microemulsions[5,6]. Then the reactions occur only in the interphase where the substrates and water can meet. The structure of the interfacial water in reverse micelles changes with the increase of $W_0$. In the case of a surfactant such as P104, added water initially hydrates the EO segments. Further added water is incorporated into the micellar cores, and the reverse micelles swell. Water in the periphery is more structured and has different physical properties, such as lower polarity, as compared to the bulk water. Only in large water droplets do the physical properties resemble those of bulk water. The polarity of water in the micelles increases with $W_0$. On the other hand, an increase in the droplet size ($W_0$) leads to the decrease of interaction between water molecules and water-philic EO segments in the polymer surfactant, thereby reducing the nucleophilicity of the interfacial water. As the hydrolysis of the substrates is sensitive to the polarity and nucleophilicity of the water, the variation of $W_0$ will affect the kinetics of the hydrolysis.

The acyl transfer reactions are commonly classified into three groups: (a) dissociative mechanism ($S_N1$), with an acylium ion intermediate concerted displacement, which can have an associative or dissociative character associative ($S_N2$), or addition-elimination, with a tetrahedral addition intermediate. The dissociative pathway will be favored by a polar solvent and a conjugative electron release effect which will stabilize the carbocationic intermediate. The associative pathway is more sensitive to the nucleophilicity of the nucleophilic agent and is favored by an electron attractive substitute.

The hydrolysis of BzCl takes place predominately through a dissociative ($S_N1$) path at larger $W_0$, and the reaction takes place fundamentally through an associative ($S_N2$) pathway at small $W_0$ in the sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/isooctane/water microemulsion. Due to the conjugative electron release by the aryl group which assists the C-Cl bond breaking, in the transition state of BzCl hydrolysis the C-Cl bond breaking has progressed further as compared to the hydrolysis of NPhCl[5,6]. In other words, the hydrolysis of BzCl proceeds via a mechanism more like $S_N1$, which involve the formation of cationic acylium and $Cl^-$. So the $k_{obs}$ of BzCl hydrolysis increases with the increase of $W_0$ as a result of the increased polarity of the water. Furthermore, the $k_{obs}$ increases slowly when the $W_0$ is very small, where the reaction may take place through an associative pathway in which decreased nucleophilicity is unfavorable to the reaction.

In the case of NPhCl, the hydrolysis takes place through a $S_N2$ path, owing to the inductive electron attraction effect of *p*-nitrophenoxy. The nucleophilic attack is the rate-determining step, and the reaction is sensitive to the nucleophilicity of water. As the $W_0$ increases, the nucleophilicity of the interfacial water decreases which is unfavorable to the hydrolysis, although the increase of water polarity is favorable to the hydrolysis. Therefore, there are two opposite factors to affect the reaction rate with increasing $W_0$. As a result, the rate constant is less sensitive to $W_0$.

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