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## Superconcentrated Hydrochloric Acid

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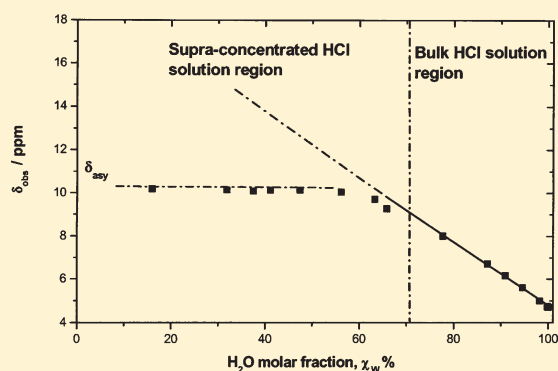
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 Supporting Information

**ABSTRACT:** We report the discovery of a potentially useful superconcentrated HCl at ambient temperature and pressure by using a simple surfactant-based reversed micelle system. Surprisingly, the molar ratios of H<sup>+</sup> to H<sub>2</sub>O (denoted as  $n_{H^+}/n_{H_2O}$ ) in superconcentrated HCl can be larger than 5, while the maximum achievable  $n_{H^+}/n_{H_2O}$  value for conventional saturated HCl aqueous solution (37 wt %) is only about 0.28. Furthermore, both NMR and FT-IR results indicate that a significant amount of HCl remains in the molecular form rather than being ionized into H<sup>+</sup> and Cl<sup>-</sup>. The superconcentrated HCl may promote some organic reactions that are not feasible by using conventional 37 wt % HCl solution. For example, addition reaction between C=C and HCl occurs in superconcentrated HCl solution without using catalysts.



## INTRODUCTION

Acid catalysis plays an important role in industrial synthesis.<sup>1–3</sup> Nowadays, more than half of catalytic processes are promoted by acids. Solid acids<sup>4–8</sup> and superacids<sup>9–11</sup> have been extensively used since the acidity of superacids and solid acids is much stronger than conventional mineral acids. However, solid acids and superacids lose the catalytic activities for those reactions where water is involved.<sup>12,13</sup> Therefore, many acid-catalyzed reactions are still carried out by using conventional strong liquid mineral acids, e.g., HCl and H<sub>2</sub>SO<sub>4</sub>.<sup>14</sup> From a kinetic point of view, increasing the concentration of mineral acid favors acid-catalyzed reactions. However, the desired increase in the concentration of many volatile acids, such as HCl, is hindered by their limited solubility at ambient temperature and atmospheric pressure. In principle, lowering the temperature or elevating the environmental pressure is helpful to achieve higher concentrations of those volatile acids.<sup>15</sup> However, such approaches are not practical in many chemical processes because it is physically not feasible in operation or may lead to unacceptable economic costs.

Surfactant-based disperse systems, such as reversed micelles, provide a unique microscopic chemical environment within their micellar aqueous phase.<sup>16,17</sup> Such a nanosized confined micellar medium often exhibits fascinating physicochemical properties.<sup>18–21</sup> Thus, microemulsions and reversed micelles have been exploited in a wide range of applications, including nanoreactors for micellar catalysis of chemical<sup>18,22–26</sup> and enzymatic reactions<sup>27–31</sup> and templates for the syntheses of nanostructured materials.<sup>32–38</sup> For example, the rates of many chemical reactions increase significantly in surfactant micelles.<sup>26,39</sup> In some cases, the rate enhancements amount to as high as 5 orders of magnitude. Thus, micelles with nanosized confined environment may produce enhanced physical and chemical outcomes that are not possible under conventional bulk states. Herein, we report the discovery of a potentially useful superconcentrated HCl at

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Table 1. Samples Reported in This Work

samples	methods	concentration of	
		surfactant (mol L <sup>-1</sup> )	acids
I	I	0.22	37 wt % HCl
II	II	1.64	gaseous HCl
III	I	0.22	67 wt % HNO <sub>3</sub>
IV	I	0.22	20 wt % DCl
V	I	0.22	20 wt % HCl

ambient temperature and pressure by using a simple reversed micelle system.

## EXPERIMENTAL SECTION

Two methods were utilized to introduce volatile acid into the organic phase.

**Method I.** HCl (37 wt %) was mixed with a benzene solution containing Aliquat 336 (trioctyl methylammonium chloride) for more than 5 min at ambient temperature. Then, the mixture was centrifuged at 10 000 rpm for 30 min, and the organic phase was collected.

**Method II.** A preset amount of water was dispersed into a benzene solution containing Aliquat 336. After ultrasonic treatment, the mixture was centrifuged at 10 000 rpm for 30 min. Afterward, dry HCl gas was bubbled into the solution for more than 1 h with vigorous stirring. Details of sample preparation in this report are summarized in Table 1.

The obtained samples were characterized by FT-IR and NMR spectroscopy. The NMR spectra were recorded on a Bruker AM 300 spectrometer operating at 300.07 and 75.46 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. Typical conditions for the proton spectra were pulse width 32°, acquisition time 5 s, FT size 32K, and digital resolution 0.3 Hz per point. For the carbon spectra: pulse width 60°, FT size 64K, and digital resolution 0.6 Hz per point. The number of scans varied from 120 to 1000 per spectrum. The signal assignments in the <sup>1</sup>H NMR spectra were performed according to our previous works.<sup>40,41</sup> The FT-IR spectra were collected on a Nicolet Magna IR 750-II Fourier transform infrared spectrometer equipped with an attenuated total reflection accessory. All the spectra were recorded at a resolution of 4 cm<sup>-1</sup>, and 32 scans were coadded. An Agilent model GC7980A series gas chromatograph coupled with a MS5975C series mass spectrometer was employed for the GC/MS analyses. Separation was performed on a 19091S-433 capillary column (30 m length, 0.25 mm ID, and 0.25 μm d<sub>f</sub>, Agilent Technologies) with helium as the carrier gas. The column temperature was initially held at 60 °C for 1 min, and then the temperature was raised to 200 °C at a rate of 10 °C min<sup>-1</sup>, followed by an isothermal period of 5 min. The injector was heated to 250 °C and was on split mode with a split ratio of 1:100.

The contents of acid and water were measured by using acid–base titration and Karl Fischer titration on a ZDJ-400 multifunctional titrimeter.

## RESULTS AND DISCUSSION

Table 2 shows the content of water and acid in samples I and II. The results show that the amount of water and acid is much higher than the limited solubility of water and HCl in benzene (Supporting Information). SAXS results indicate that the organic phase is not homogeneous but contains microscopic reversed

Table 2. Contents of Water and HCl in Samples I and II

samples	content of water		<i>n</i> <sub>HCl</sub> / <i>n</i> <sub>H<sub>2</sub>O</sub>
	(mmol g <sup>-1</sup> )	content of HCl (mmol g <sup>-1</sup> )	
I	0.33	0.58	1.7
II	0.58	3.08	5.7

micelles (Supporting Information). Thus, most water and HCl are concentrated in reverse micelles. After removing the contribution of HCl dissolved in benzene, the molar ratios between HCl and water (*n*<sub>HCl</sub>/*n*<sub>H<sub>2</sub>O</sub>) in the reverse micelle are listed in Table 2. The *n*<sub>HCl</sub>/*n*<sub>H<sub>2</sub>O</sub> values for samples I and II range from 1.7 to 5.3. In comparison, the *n*<sub>HCl</sub>/*n*<sub>H<sub>2</sub>O</sub> ratio for a conventional 37 wt % HCl solution is only 0.28. Thus, the concentrations of HCl in the reversed micelle are much higher than the conventional saturated HCl solution. Therefore, the benzene/Aliquat 336/H<sub>2</sub>O/HCl mixtures are called superconcentrated HCl and denoted as SC-HCl.

We notice that the *n*<sub>HCl</sub>/*n*<sub>H<sub>2</sub>O</sub> values in samples I and II are larger than 1. There is not enough water to accommodate H<sup>+</sup> if every HCl produces one H<sup>+</sup>. Moreover, the *n*<sub>HCl</sub>/*n*<sub>H<sub>2</sub>O</sub> values in some cases are even greater than 2. That is to say, the amount of water is not enough even if H<sub>4</sub>O<sub>2</sub><sup>+</sup> exists (no H<sub>4</sub>O<sub>2</sub><sup>+</sup> is reported in the literature). Therefore, some HCl must remain as unionized molecules in the reverse micelles.

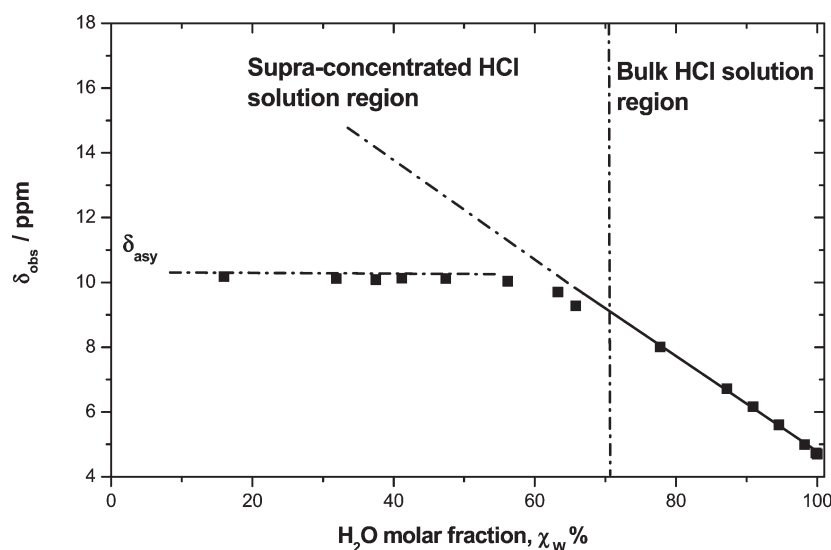
To test whether or not an unionized HCl molecule indeed exists, NMR and FT-IR spectroscopic studies were performed. Due to fast chemical exchange, the <sup>1</sup>H NMR signals of water and hydrated H<sup>+</sup> merge into one peak, whose chemical shift (denoted as δ<sub>obs</sub>) exhibits a downfield shift as the concentration of H<sup>+</sup> increases.

Figure 1 depicts δ<sub>obs</sub> as a function of the molar fraction of water (χ<sub>w</sub>, where χ<sub>w</sub> = *n*<sub>w</sub>/(*n*<sub>w</sub> + *n*<sub>H<sup>+</sup></sub>)). A good linear relationship can be observed in bulk HCl solution (χ<sub>w</sub> > 78%). In HCl solution, the exchangeable proton occurs in two states: one is water whose chemical shift is denoted as δ<sub>w</sub> (4.67 ppm), and the other is H<sup>+</sup> whose chemical shift is denoted as δ<sub>H</sub>. The linear relationship between δ<sub>obs</sub> and χ<sub>w</sub> can be expressed as

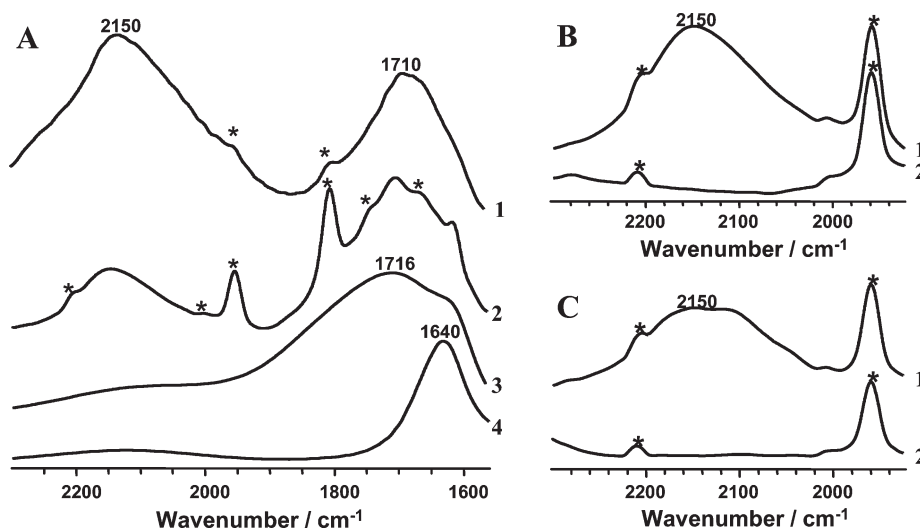
$$\delta_{\text{obs}} = (1 - \chi_w)\delta_H + \chi_w\delta_w \quad (1)$$

where δ<sub>w</sub> is 4.67 ppm and δ<sub>H</sub> is extrapolated to be 19.42 ppm.

A severe and systematic deviation from the linear relationship between δ<sub>obs</sub> and χ<sub>w</sub> is observed for SC-HCl (χ<sub>w</sub> < 78%). In fact, δ<sub>obs</sub> asymptotically approaches a constant (δ<sub>asy</sub>) as χ<sub>w</sub> decreases further. That is to say, more than two chemical species take part in the chemical exchange, and most H<sup>+</sup> are entrapped by certain chemical species. The resultant new product dominates in SC-HCl. There are five chemical species: H<sub>2</sub>O, benzene and methyl trioctyl ammonium, H<sup>+</sup>, and Cl<sup>-</sup>. Water and H<sup>+</sup> are already involved in the chemical exchange. Although benzene has considerable ability of interacting with H<sup>+</sup>, it cannot accommodate too much H<sup>+</sup>. Methyl trioctyl ammonium is a cation with a hydrophobic surface and cannot bind H<sup>+</sup>. Thus, only Cl<sup>-</sup> is left to interact with H<sup>+</sup>. The result suggests that H<sup>+</sup> binds with Cl<sup>-</sup> to form an unionized HCl molecule. The hypothesis of the formation of the HCl molecule in SC-HCl is further supported by FT-IR spectroscopic studies. Figure 2A shows the FT-IR spectra of SC-HCl (Samples I and II), H<sub>2</sub>O, and 37 wt % HCl. A strong band at 2150 cm<sup>-1</sup> can be observed in the FT-IR spectra of Samples I and II. The band is much sharper and cannot be assigned to the combination band of water. A possible assignment



**Figure 1.** Chemical shift ( $\delta_{\text{obs}}$ ) of the exchangeable proton varies with the molar fractions of  $\text{H}_2\text{O}$  ( $x_w$ ). (A good linear relationship can be observed in bulk HCl solution ( $x_w > 78\%$ ). However, a severe and systematic deviation from the linear relationship between  $\delta_{\text{obs}}$  and  $x_w$  is observed for the superconcentrated HCl ( $x_w < 78\%$ ). The  $\delta_{\text{obs}}$  asymptotically approaches a constant ( $\delta_{\text{asy}}$ ) as  $x_w$  decreases further.)



**Figure 2.** (A) FT-IR spectra of SC-HCl (line 1 Sample II; line 2 Sample I), 37 wt % HCl (line 3), and water (line 4). A strong band at  $2150\text{ cm}^{-1}$  can be observed in the spectra of SC-HCl. (B) FT-IR spectra of sample I (line 1) and superconcentrated  $\text{HNO}_3$  (line 2). The  $2150\text{ cm}^{-1}$  band is absent in the spectra of the superconcentrated  $\text{HNO}_3$ . (C) FT-IR spectra of SC-HCl ( $n_{\text{HCl}}/n_{\text{H}_2\text{O}} = 0.63$ , line 1) and SC-DCl ( $n_{\text{DCl}}/n_{\text{H}_2\text{O}} = 0.52$ , line 2). The  $2150\text{ cm}^{-1}$  band occurs in the FT-IR spectrum of the SC-HCl but disappears in the FT-IR spectrum of SC-DCl.

is that the  $2150\text{ cm}^{-1}$  band is attributed to H–Cl stretching vibration under the influence of a hydrogen bond. To our knowledge, no H–Cl stretching band has been observed in conventional bulk HCl aqueous solution since HCl completely ionizes into  $\text{H}^+$  and  $\text{Cl}^-$ . Ndongmouo<sup>42</sup> used DFT calculation to simulate the H–Cl stretching vibration in a model system and found that the H–Cl stretching vibration under the presence of a hydrogen bond of water is around  $2250\text{ cm}^{-1}$ . This result is quite close to the experimental observed band at  $2150\text{ cm}^{-1}$  in the SC-HCl solution. Thus, it is reasonable to assign the peak at  $2150\text{ cm}^{-1}$  as a H–Cl stretching band under the influence of hydrogen bonds. Further experimental results support the above assignment. We have used benzene containing Aliquat 336 to extract saturated  $\text{HNO}_3$  solution (Sample III). The calculated

$n_{\text{HNO}_3}/n_{\text{H}_2\text{O}}$  is 3.8, while  $n_{\text{HNO}_3}/n_{\text{H}_2\text{O}}$  for saturated  $\text{HNO}_3$  (67 wt %) is only 0.52. That is to say, Sample III is also a superconcentrated acid solution. However, the  $2150\text{ cm}^{-1}$  band is not observable in the FT-IR spectrum of Sample III (Figure 2B). The only difference between Samples I and II and Sample III is that  $\text{Cl}^-$  is replaced by  $\text{NO}_3^-$  in Sample III. Thus, the  $2150\text{ cm}^{-1}$  band must be related to  $\text{Cl}^-$ . In another experiment, SC-HCl can also be obtained by using an Aliquat 336/benzene mixture to extract 20 wt % HCl. The  $n_{\text{HCl}}/n_{\text{H}_2\text{O}}$  value turns out to be 0.63, and the  $2150\text{ cm}^{-1}$  band is also observable in the FT-IR spectrum. However, the  $2150\text{ cm}^{-1}$  band disappears in a sample that is prepared by extracting 20 wt % DCl with the Aliquat 336/benzene mixture ( $n_{\text{DCl}}/n_{\text{H}_2\text{O}}$  is 0.52), suggesting that the  $2150\text{ cm}^{-1}$  band is also related to  $\text{H}^+$  (Figure 2C). The above

Table 3. SC-HCl Samples with Variable Temperatures

temperature (°C)	content of water (mmol/g)	content of HCl (mmol/g)	$n_{\text{HCl}}/n_{\text{H}_2\text{O}}$
10 °C	0.61	4.55	7.5
25 °C	0.60	4.24	7.1
40 °C	0.66	3.70	5.6
60 °C	0.73	3.10	4.3

Table 4. SC-HCl Samples with Variable Concentration of Aliquat 336

concentration of Aliquat 336 (wt%)	content of water (mmol/g)	content of HCl (mmol/g)	$n_{\text{HCl}}/n_{\text{H}_2\text{O}}$
10	$6.67 \times 10^{-2}$	0.82	12
30	0.33	2.04	6.2
50	0.81	3.32	4.1
60	0.61	3.77	6.2
70	0.55	4.05	7.4

results demonstrate that the  $2150\text{ cm}^{-1}$  band is related to both  $\text{H}^+$  and  $\text{Cl}^-$ , while neither  $\text{H}^+$  nor  $\text{Cl}^-$  alone can produce this IR signal. Thus, the  $\text{H}-\text{Cl}$  bond must form, which is manifested by the  $2150\text{ cm}^{-1}$  band in the FT-IR spectrum of superconcentrated HCl.

To enhance our understanding on the role of reverse micelles in the formation of SC-HCl, we have prepared the SC-HCl samples when system temperature, the concentration, and types of surfactant are variable.

First, we tried to prepare SC-HCl samples under different temperatures. Aliquat 336 was dissolved in benzene, and the concentration of Aliquat 336 in the solution was  $1.64\text{ mol L}^{-1}$ . Water was dispersed into the benzene solution. After ultrasonic treatment, the mixture was centrifuged at 10 000 rpm for 30 min. Afterward, dry HCl gas was bubbled into the solution for more than 1 h with vigorous stirring. During this process, the flask containing the benzene solutions was soaked in a water bath or water–ice mixture so that the solution can be equilibrated at different temperatures that ranged from 10 to 60 °C. The results of acid–base and Karl Fischer titration indicate that SC-HCl can be obtained when the temperature is between 10 and 60 °C (Table 3). Moreover, the  $n_{\text{HCl}}/n_{\text{H}_2\text{O}}$  values decrease with increasing temperature.

Second, we tried to prepare SC-HCl when the concentration of surfactant is variable. A different amount of Aliquat 336 was dissolved in benzene so that the concentration of the surfactant ranged from 10 wt % to 70 wt %. Then water was added and dispersed in the benzene solutions under supersonic treatment. The mixture was centrifuged at 10 000 rpm for 30 min. Afterward, dry HCl gas was bubbled into the solution for more than 1 h with vigorous stirring. Both acid–base and Karl Fischer titration were performed on the obtained samples (Table 4). The results demonstrate that SC-HCl samples are obtained when the concentration of Aliquat 336 ranges from 10 wt % to 70 wt %.

In addition, we have also performed some preliminary studies on utilizing different surfactant to prepare SC-HCl. We tried to use tributyl phosphate as the surfactant to prepare SC-HCl. First, tributyl phosphate was dissolved in heptane, and the concentration of tributyl phosphate was 30 wt %. Then, HCl (37 wt %) was mixed with the benzene solution of tributyl phosphate for more

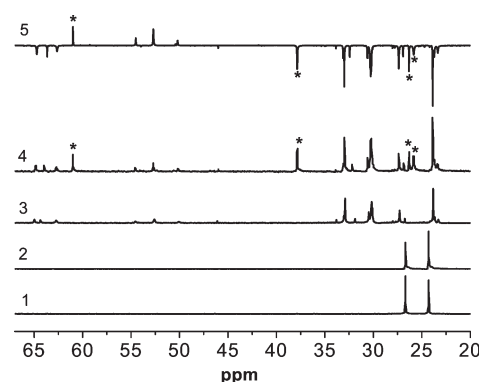


Figure 3.  $^{13}\text{C}$  NMR spectra of SC-HCl/cyclohexene and related systems: 1, cyclohexene; 2, organic phase of cyclohexene/37 wt % HCl mixture; 3, SC-HCl; 4, SC-HCl/cyclohexene mixture; 5, DEPT spectrum.

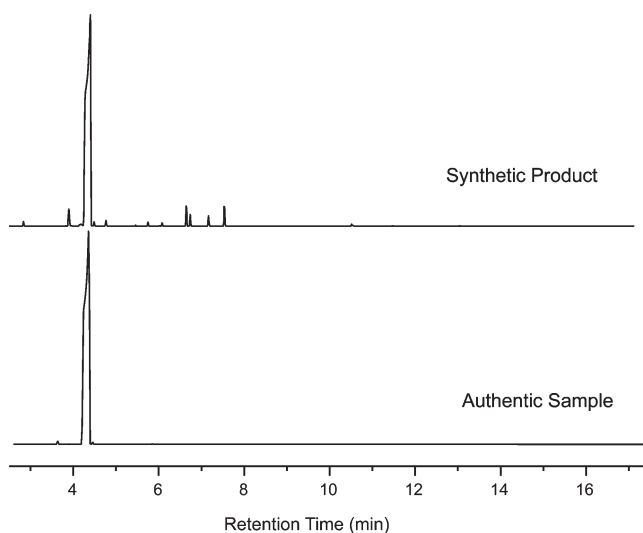


Figure 4. Total ion chromatogram of the synthetic product and 1-Cl-cyclohexane authentic sample.

than 5 min at ambient temperature. Then the mixture was centrifuged at 10 000 rpm for 30 min, and the organic phase was collected. Results of acid–base and Karl Fischer titration indicate that the  $n_{\text{HCl}}/n_{\text{H}_2\text{O}}$  value was 0.89. Additionally, we prepared benzene solution of tributyl phosphate in which the concentration of tributyl phosphate is 80 wt %. About 1 wt % of water was added and dispersed in the solutions. After ultrasonic treatment, the mixture was centrifuged at 10 000 rpm for 30 min. Afterward, dry HCl gas was bubbled into the benzene solution for more than 1 h under vigorous stirring. Both acid–base and Karl Fischer titration were performed, and the  $n_{\text{HCl}}/n_{\text{H}_2\text{O}}$  value turned out to be 5.5.

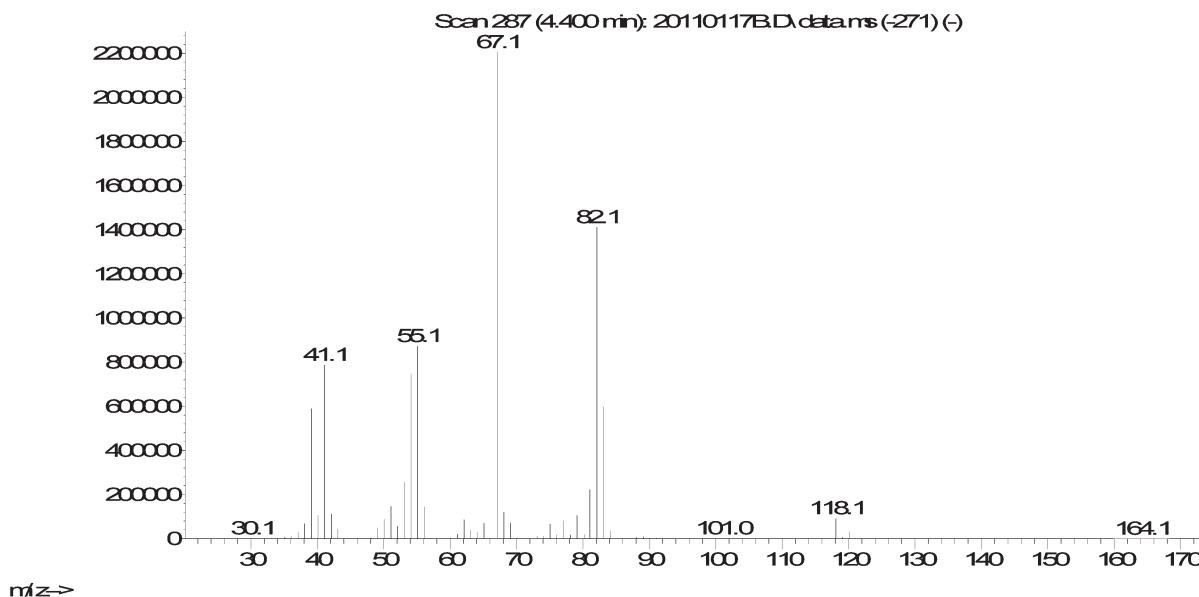
The above results showed that SC-HCl can be prepared in a reversed micelle where the temperature, the type, and concentration of surfactant are variable. Further work is still being carried out to enhance our understanding on the physical-chemical mechanism of the SC-HCl formation.

SC-HCl may provide potential opportunities to promote organic chemical reactions that are not feasible in conventional conditions. For example, we have added cyclohexene into a SC-HCl whose  $n_{\text{HCl}}/n_{\text{H}_2\text{O}}$  is 5.26. The  $^{13}\text{C}$  NMR spectrum of the



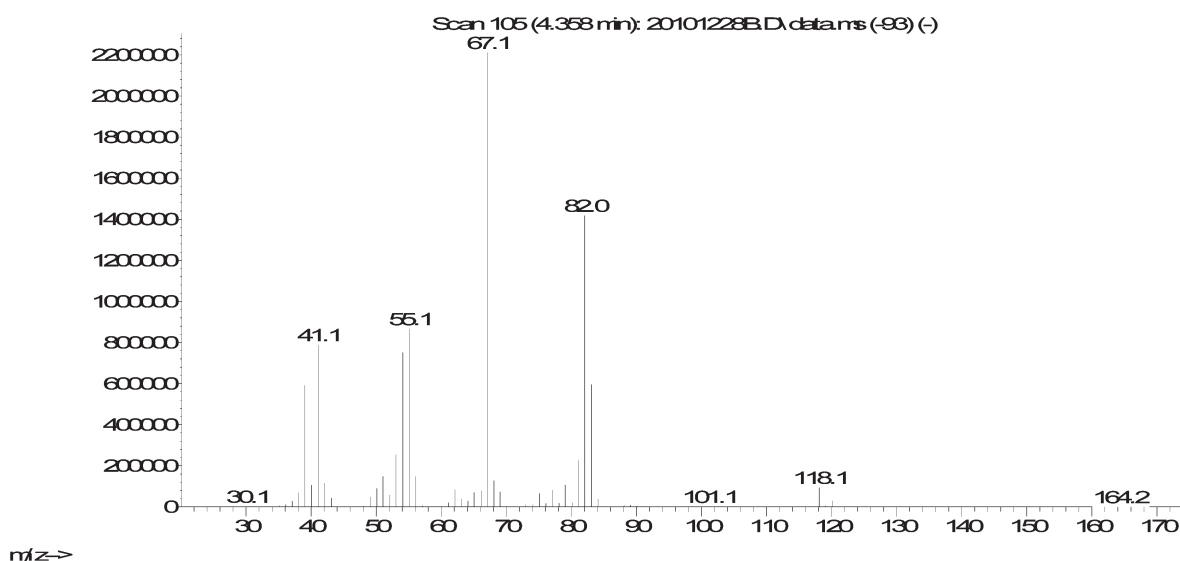
Synthetic product, the component whose retention time is 4.40min

Abundance



1-Cl-cyclohexane authentic sample, the component whose retention time is 4.40min

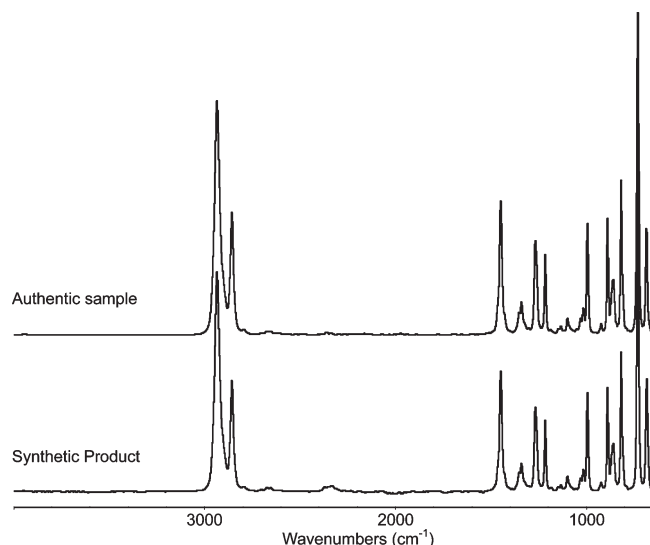
Abundance



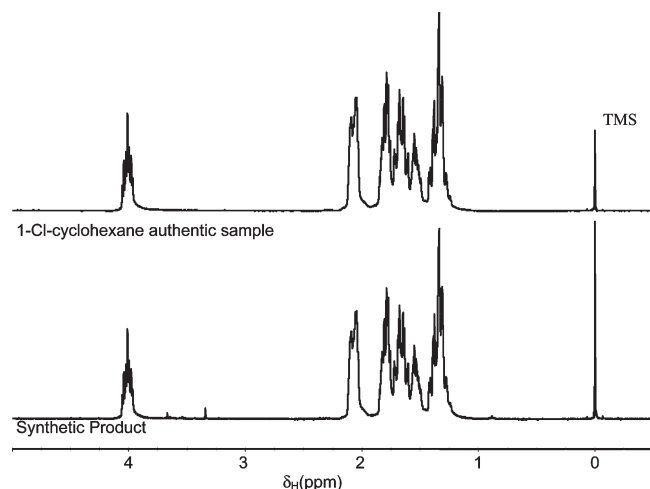
**Figure 5.** Mass spectra of the main component from the synthetic product and 1-Cl-cyclohexane authentic sample.

SC-HCl/cyclohexene mixture was recorded (Figure 3). For comparison, the  $^{13}\text{C}$  NMR spectra of the organic phase of cyclohexene/37 wt % HCl mixture, SC-HCl, and cyclohexene were also measured. Except for the peaks of cyclohexene, no new peak appears in the  $^{13}\text{C}$  NMR spectrum of cyclohexene/37 wt % HCl mixture. Nevertheless, four new peaks at 61.0, 37.9, 26.3, and 25.8 ppm appear in the  $^{13}\text{C}$  NMR spectrum of the cyclohexene/SC-HCl mixture. We propose the new peaks are from 1-Cl-cyclohexane, the product of the addition reaction between cyclohexene and superconcentrated HCl. The peak at 61.0 ppm is assigned to the carbon atom of the  $\text{CHCl}$  group. The peak at 37.8 ppm is attributed to the methylene carbon atoms that directly link to the  $\text{CHCl}$  group. The peaks at 26.3 and 25.8

ppm are from two other types of  $\text{CH}_2$  groups. Further experimental results confirm the occurrence of 1-Cl-cyclohexane. First, in DEPT135 experiment, the peak at 61.0 ppm is positive, while the peaks at 37.8, 26.3, and 25.8 ppm are negative, supporting the above assignment. Second, a standard  $^{13}\text{C}$  NMR spectrum of 1-Cl-cyclohexane in  $\text{CDCl}_3$  has four peaks at 60, 36, 25.3, and 24.9 ppm that are quite close to the four new peaks found in the  $^{13}\text{C}$  NMR spectrum of the superconcentrated HCl/cyclohexene mixture (Supporting Information). To get more products and simplify separation process for further structural characterization, we modified the reaction conditions. First, a mixture of 42 g of cyclohexene and 24 g of benzene was used to dissolve 56 g of Aliquat 336. A preset amount of water (about 2 wt %) was



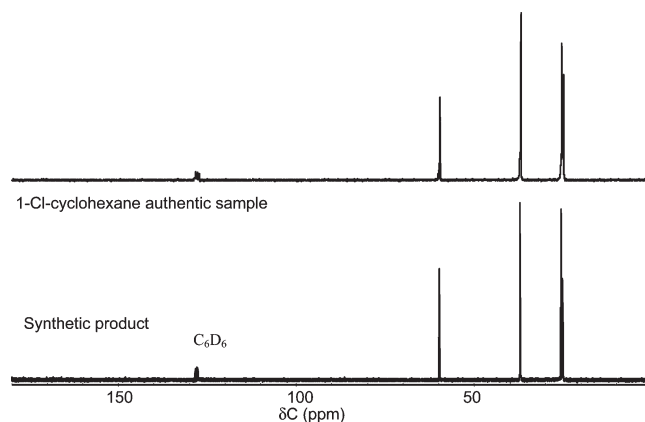
**Figure 6.** FT-IR spectra of the synthetic product and 1-Cl-cyclohexane authentic sample.



**Figure 7.**  $^1\text{H}$  NMR spectra of the synthetic product and 1-Cl-cyclohexane authentic sample.

dispersed into the solution under ultrasonic treatment. Afterward, HCl gas was bubbled into the solution at room temperature with vigorous stirring. During the reaction,  $n_{\text{HCl}}/n_{\text{H}_2\text{O}}$  ranges from 4.92 to 6.47, demonstrating that the reaction is performed under the superconcentrated HCl condition. The resultant mixture was first distilled at 100 °C (oil bath temperature) at ambient pressure to remove benzene and unreacted cyclohexene and then distilled at reduced pressure and 110 °C (oil bath temperature) to collect chlorocyclohexane. The product was characterized by NMR, FT-IR, and GC-MS. For comparison, chlorocyclohexane in AR grade was used as an authentic sample.

The total ion chromatograms for the GC-MS analysis of the product and chlorocyclohexane are shown in Figure 4. A compound at a retention time of 4.4 min appears as the strongest peak in the total ion chromatogram of the product and chlorocyclohexane. Furthermore, this compound is identified as 1-Cl-cyclohexane by comparison of its chromatographic behavior and mass spectra with those of an authentic sample. The mass spectra of the component whose retention time is 4.4 min and



**Figure 8.**  $^{13}\text{C}$  NMR spectra of the synthetic product and 1-Cl-cyclohexane authentic sample.

1-Cl-cyclohexane are almost identical (Figure 5), supporting that 1-Cl-cyclohexane was obtained.

In addition, FT-IR spectra and  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the product and authentic sample of 1-Cl-cyclohexane are shown in Figures 6, 7, and 8. The FT-IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectra of the product and 1-Cl-cyclohexane are almost identical, providing further evidence that 1-Cl-cyclohexane, the product of addition reaction between  $\text{C}=\text{C}$  and HCl, is produced. This result suggests that SC-HCl provides an environment with high concentration of  $\text{H}^+$ ,  $\text{Cl}^-$ , and HCl and promotes the addition reaction of HCl onto  $\text{C}=\text{C}$  effectively.

In summary, we report a new approach to prepare superconcentrated HCl. Both NMR and IR results demonstrate that part of HCl molecules do not ionize into  $\text{H}^+$  and  $\text{Cl}^-$ . The superconcentrated HCl may provide opportunities to promote organic chemical reactions that have not been feasible in a conventional medium.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** The results of SAXS and standard  $^{13}\text{C}$  NMR spectra of 1-Cl-cyclohexane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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