

Capture of Carbon Dioxide by Cucurbit[7]uril Complex

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Abstract—A supramolecular approach to CO₂ capture by cucurbit[7]uril (CB[7]) complex was developed. NH₂(CH₂)₆NH₂·CB[7] complex can convert CO₂ to bicarbonate product exclusively and faster in solution due to the deshielding effect, thereby providing a green absorbent to CO₂ with regard to high stability, non-corrosiveness and convenient transportation.

Keywords—carbon dioxide; cucurbituril; capture; supramolecular catalysis

I. INTRODUCTION

CO₂ capture and fixation have called worldwide attention not only due to the increasing environmental concerns, but also in view of the carbon resource utilization [1]. Traditional sorbents of CO₂ include aqueous amines, which react with CO₂ rapidly at room temperature and can be released easily by gentle heating (60-110 °C) or simply by addition of HCl or TFA [2]. This reversible conversion leads to controllable capture and release of CO₂ from gas streams. However most of the amines are corrosive to equipment and degrade through oxidation [3], which severely restricts the wide application in CO₂ capture. To solve the problems, amine-modified solid sorbents supported on silica gels [4], molecular sieves and polymers [5] have been designed and synthesized. Herein we introduced a new supramolecular approach to capture CO₂ by cucurbituril complex, in combination with reversible CO₂-amine reaction [6].

Cucurbit[n]urils (CB[n]) have become important supramolecular macrocyclic hosts after crown ether, cyclodextrin and calixarene [7]. Ever since Mock firstly reported that 1,3-dipolar cycloaddition could be accelerated by a factor of 5.5×10^4 under the influence of CB[6] [8], applications of CB[n] as catalyst have been investigated in a variety of reactions, such as hydrolysis, solvolysis, desilylation, thiol-disulfide interchange, H/D exchange, oxidation and photoreactions [9]. Due to the complexation within CB cavity, chemical reactivity of the guests could be altered, resulting in rate change, selectivity change and even new products.

In virtue of the unique characteristics of recognition and assembly for supramolecular macrocyclic host structures, amine-modified calixarene [10] and crown ethers [11] have been designed for construction of novel nanostructures and materials. In this work, we revisited the CO₂-amine chemistry and developed supramolecular approach to CO₂ capture catalyzed by CB[7] (Figure 1), without resort to the chemical modification step of amino group.

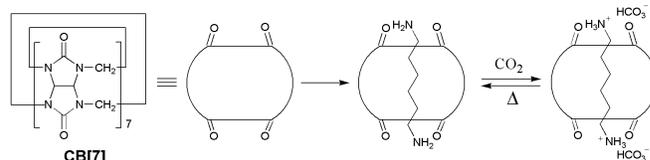


Figure 1. CO₂ capture by CB[7]-amine complex.

II. EXPERIMENTAL

A. Materials and Apparatus

Cucurbit[7]uril was synthesized using a published procedure [12] and characterized by NMR prior to use. The highly pure CO₂ (99.999%) was obtained from local supplier. ¹H and ¹³C NMR spectra were recorded on Bruker DRX-400 spectrometer for ¹H at 400 MHz and for ¹³C at 100 MHz.

B. Preparation of the CB[7] Complex

NH₂(CH₂)₆NH₂·CB[7] complex was readily prepared by mixing solid CB[7] (100 mg) with excess of 1,6-hexanediamine (2.000 g) at 50 °C for 3.5 h. After filtration, the uncomplexed amine was washed out thoroughly with methanol. The white powder was dried under vacuum at 70 °C for 3 h (49% yield based on CB[7]).

C. CO₂ Reaction in Aqueous Solution

NH₂(CH₂)₆NH₂ or NH₂(CH₂)₆NH₂·CB[7] complex (0.004-0.05 M) was dissolved in D₂O in a 5 mm NMR tube. CO₂ was then bubbled through the solution at 25 °C with a flow rate of 10 mL/min as regulated by flow meter. The CO₂ reactions were monitored by ¹H and ¹³C NMR spectra.

III. RESULTS AND DISCUSSION

As reported, amine reacts with CO₂ to form carbamate by nucleophilic reaction as in Eq. (1) and bicarbonate by acid-base neutralization as in Eq. (2), whereas decomposition of carbamate with excess of CO₂ also leads to bicarbonate as in Eq. (3) [2]. The reactions of amines with CO₂ in water for a long time are inclined to form bicarbonate as primary product, however the conversions are hardly complete with a little side product of carbamate, for they are equilibrium reactions. In our model experiment, NH₂(CH₂)₆NH₂ reacted with CO₂ in aqueous solution, leading to carbamate product first and then bicarbonate, which were demonstrated by the appearance of carbonyl signals on ¹³C NMR spectra at δ 164.5 and 159.9 ppm, respectively.

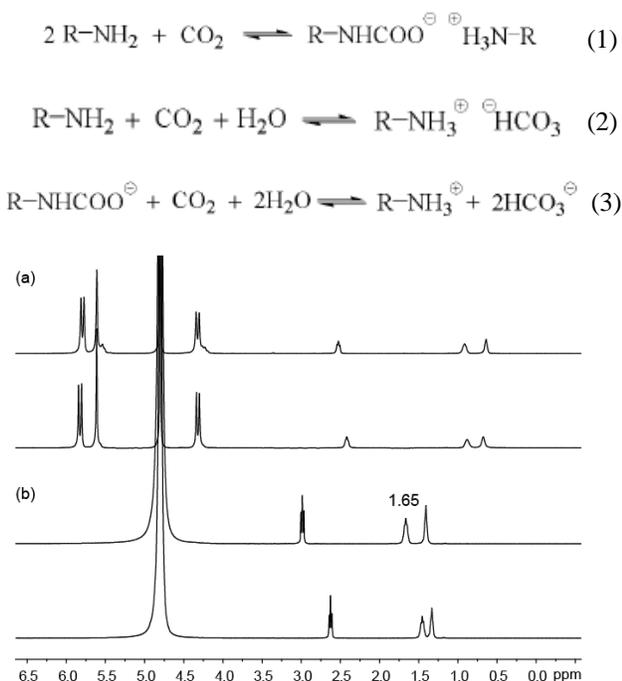


Figure 2. ^1H NMR spectra of (a) $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{<CB[7]}$ and (b) $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ in D_2O before (bottom) and after (top) bubbling CO_2 (10 mL/min) to give the final bicarbonate products.

In contrast, the $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{<CB[7]}$ complex was synthesized and characterized by ^1H NMR (Figure 2), where 1:1 host-guest ratio could be derived from the integration and the resonance signals assigned to amine moving upfield indicate their positioning within the cavity of CB[7]. For reaction of $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{<CB[7]}$ complex with CO_2 in aqueous solution, the new resonance signal on ^{13}C NMR spectrum at δ 159.8 ppm was assigned to bicarbonate as the only product of CO_2 fixation, while carbamate product was not detected.

To further verify the different reaction pathways for bound amine and free amine, $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{<CB[7]}$ complex was mixed with $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ in 1:1 ratio, whereby their reaction processes with CO_2 have been monitored in one pot by ^1H NMR (Figure 3). It was found that component of $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ reacted with CO_2 to form carbamate predominantly at 45 s, which nearly transformed to bicarbonate at 70 s (Figure 3a). The proton signals of bicarbonate product corresponding to free amine shifted from 1.35, 1.46, 2.65 ppm to 1.39, 1.65, 2.98 ppm, among which the signal at 1.65 ppm was diagnostic of the bicarbonate formation (Figure 2). Figure 3b shows the yield of bicarbonate product for free amine increased from 25% at 45 s to above 90% at 70 s based on integration of the resonance signal at 1.65 ppm, while the yield of carbamate intermediate decreased accordingly based on integration of the resonance signal at 1.25-1.52 ppm deducted by that at 2.98 ppm. However for component of $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{<CB[7]}$ complex, still no carbamate intermediate could be detected under the same concentration. The proton signals of bicarbonate product corresponding to bound amine shifted

from 0.67, 0.86, 2.37 ppm to 0.61, 0.89, 2.51 ppm, whereas the signal shifts appeared and the conversion stayed complete since 45 s based on integration of the resonance signal at 0.61, 0.89 or 2.51 ppm (Figure 3b), suggesting a different reaction pathway not involving intermediate of carbamate.

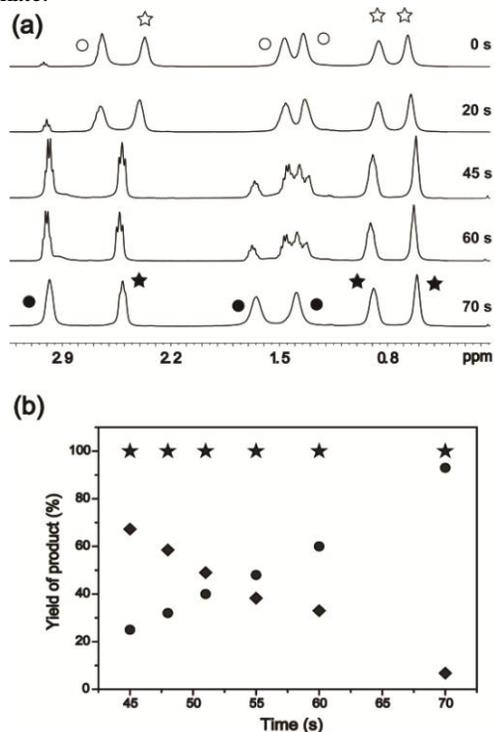


Figure 3. (a) ^1H NMR spectra of $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{<CB[7]}$ and $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ (1:1, 0.05 M) in D_2O when bubbling CO_2 (10 mL/min). Signals for free amine (o), bound amine (☆) and their bicarbonate products (in solid form) are highlighted. (b) Yields of carbamate product (◆) and bicarbonate product (●) for free amine, and bicarbonate product (★) for bound amine vs time.

The absence of carbamate product for bound amine whether or not in a mixture with free amine could be mostly ascribed to the deshielding effect [13,14] in that nucleophilicity of bound amine to attack CO_2 decreases as influenced by the electronegative portal oxygens, while the steric effect also inhibits the formation of carbamate to some extent. On the other hand, increased electrophilicity of bound amine caused by the deshielding effect favors the acid-base neutralization towards bicarbonate product, thus resulting in higher selectivity and faster reaction rate for bound amine compared to free amine.

IV. CONCLUSIONS

In summary, a supramolecular approach to CO_2 capture catalyzed by CB[7] was reported for the first time. $\text{NH}_2(\text{CH}_2)_6\text{NH}_2\text{<CB[7]}$ complex can convert CO_2 to bicarbonate product exclusively and faster in solution. The deshielding effect of CB[7] on the encapsulated amine increases the selectivity for bicarbonate over carbamate and accelerates CO_2 fixation towards bicarbonate. Thereby a

green absorbent to CO₂, was provided, regarding high stability, non-corrosiveness and convenient transportation.

ACKNOWLEDGMENTS

This project was supported by the Fundamental Research Funds for the Central Universities, the National Natural Science Foundation of China (No. 21003123), and a grant from Advanced Programs for the Returned Overseas Chinese Scholars, Ministry of Human Resources and Social Security.

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