CO₂ Capture

Equimolar CO₂ Capture by N-Substituted Amino Acid Salts and Subsequent Conversion**

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The gas responsible for climate change, CO_2 , is the subject of increased attention in both academic and industrial research.^[1] Since controlling anthropogenic CO_2 emission and further reducing the accumulation of CO_2 is emerging as an urgent and challenging research topic, extensive efforts are being devoted to carbon capture and storage/sequestration (CCS).^[2] In this context, the invention and modification of new chemicals that can efficiently, selectively, and economically absorb and separate CO_2 from the exhaust formed from the burning of fossil fuels appears essential to realize a practical CCS process.

Conventional technology for the industrial capture of CO_2 largely relies on employing aqueous solution of amines.^[3] In academic research, many amine-based scrubbing agents have been developed for various technologies and processes.^[4] However, there are inherent drawbacks generally associated with amine absorbents, namely the requirement of two amine units to capture one CO_2 molecule owing to the formation of ammonium carbamate (Scheme 1 a); this increases the energy required for regeneration. This undesired 2:1 stoichiometry would be a crucial barrier for improving the capacity of such amine-based CO_2 absorbents.

Several strategies have been proposed for the equimolar chemisorption of CO₂ with an amine absorbent. The groups led by Jessop,^[5] Dai,^[6] and others^[7] have developed reversible CO₂ capture utilizing a strong nitrogen-containing base in conjunction with a proton donor. Meanwhile, amidophosphoranes were also proved to be capable of capturing one equivalent of CO₂ through the insertion of CO₂ into a P–N bond, resulting in the generation of carbamatophosphoranes.^[8] Despite the high absorption capacity of amidophosphoranes at a 1:1 stoichiometry, additional inter-/intramolecular functional groups such as hydroxy-, amino-, phosphorus-

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- [**] This work was supported financially by the National Natural Sciences Foundation of China (no. 21172125), the Ministry of Science and Technology (2012BAD32B10), the "111" Project of the Ministry of Education of China (project no. B06005), and the Committee of Science and Technology of Tianjin.
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201205362.



O: bulky alkyl substituent

Scheme 1. a) Conventional amine-based scrubbing for CO_2 capture through the ammonium carbamate pathway; b) CO_2 capture via the formation of the carbamic acid rather than the ammonium carbamate by sodium *N*-alkylglycinate in PEG.

containing species were essentially required to form the carbamate/carbonate. Very recently, Brennecke and co-workers^[9] designed an ionic liquid (IL) comprising an aminofunctionalized anion and a long-chain alkyl phosphonium cation to capture CO₂ in favor of formation of carbamic acid; they approached a high capacity of up to almost 1 mole of CO₂ per mole of IL. Despite such great advances, the development of efficient CCS processes continues to be appealing. The ultimate goal is a simple, easily prepared, biocompatible/biodegradable absorbent with high CO2 capacity up to a 1:1 stoichiometry, and thus a lower energy requirement in the desorption step. In this context, we found that readily available amino acid salts with a bulky N substituent have an extremely high capacity approaching almost equimolar absorption in poly(ethylene glycol) (PEG) solution (Scheme 1b). Steric-hindrance-controlled CO₂ absorption is assumed to proceed via the carbamic acid rather than the ammonium carbamate, thus resulting in equimolar absorption and improved ease of desorption in comparison with conventional amine absorbents. In particular, the captured CO₂ could be an activated species that could undergo subsequent conversion to give valuable compounds smoothly rather than going through a desorption cycle.

Sodium *N*-alkylglycinates and -alaninates^[10] were investigated to test our proposal about steric-hindrance-controlled CO₂ absorption (Table 1). PEG was selected as a suitable solvent because the flexible poly(ethylene oxide) chain could coordinate with alkali-metal cations, thus leading to improved capacity for counterions.^[11] In particular, PEG₁₅₀ (triethylene glycol, $M_w = 150$ Da) showed poor CO₂ sorption capacity alone, implying that only physical interaction between PEG and CO₂ was observed (Table 1, entry 1). As expected, nonmodified sodium glycinate captured CO₂ in a manner similar to aqueous amines, by forming the ammonium carbamate in a stoichiometry of one CO₂ molecule to two amino groups (Table 1, entry 2); this salt was detected by

<i>Table 1:</i> CO ₂ absorption using various amino acid salts. ^[a]				
H ₂ N ONa	iPr ^{-N} ONa	nPr ^{-N} ONa	a tBu ^{-N} _ONa	
NH ₂ -GlyNa	<i>i</i> PrNH-GlyNa	<i>n</i> PrNH-GlyNa	tBuNH-GlyNa	
Cy ^{-H} ONa	<i>i</i> Pr ⁻ N ^O ONa	nPr O nPr N ONa	a ^{iPr} N ONa	
CyNH-GlyNa	iPrNH-AlaNa	<i>n</i> Pr ₂ N-GlyNa	β-iPrNH-AlaNa	
Entry Ab	sorbent	t [min] ^[b]	CO ₂ absorption ^[c]	

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1	-	20	0.035 ^[d]
2	NH ₂ -GlyNa	20	0.43
3	<i>i</i> PrNH-GlyNa	25	0.91
4	<i>n</i> PrNH-GlyNa	30	0.59
5	tBuNH-GlyNa	25	0.85
6	CyNH-GlyNa	25	0.68
7	iPrNH-AlaNa	30	0.73
8	<i>n</i> Pr₂N-GlyNa	30	0.48
9	β- <i>i</i> PrNH-AlaNa	15	0.65
10	NaOAc	20	trace
11 ^[e]	<i>i</i> Pr ₂ NH/NaOAc	20	0.53

[a] Conditions: PEG_{150} (12 mmol), absorbent (3 mmol), 25 °C. [b] Time required to reach absorption equilibrium. [c] Moles of CO_2 captured per mole of absorbent and absorption by PEG_{150} is subtracted. [d] Moles of CO_2 captured per mole of PEG_{150} . [e] Conditions: PEG_{150} (12 mmol), *i*Pr₂NH (3 mmol), NaOAc (3 mmol), 25 °C.

¹³C NMR spectroscopy.^[12a] To our delight, introducing an isopropyl substituent at the α -amino group greatly enhanced the CO_2 capacity, which approached the 1:1 stoichiometry expected based on the theoretical arguments (Table 1, entry 3). In this context, the ¹³C NMR evidence could exclude the carbamate pathway.^[12b] The CO₂ absorption of *N-n*-propyl glycinate was inferior to that of the N-isopropyl counterpart (Table 1, entry 3 vs. entry 4). Increasing the size of the N substituent did not improve the absorbance further (Table 1, entry 5 vs. entry 3). Increased viscosity could have a detrimental effect in the case of sodium N-cyclohexyl glycinate (Table 1, entry 6). An additional methyl group at the position α to the N atom could be interfere with the interaction with CO_2 (Table 1, entry 7). However, the tertiary amino counterpart, which lacks an N-H group, demonstrates low CO₂ capacity (Table 1, entry 8). A substituted β -amino acid salt showed lower CO_2 capacity than its α -amino analogue (Table 1, entry 9 vs. entry 3). The binding of CO₂ through the weakly alkaline carboxyl group can be ruled out because of the negligible absorption of NaOAc (Table 1, entry 10). Furthermore, a 1:1 mixture of *i*Pr₂NH and NaOAc captured 0.53 mole of CO_2 per mole of amine, suggesting that the carboxylate moiety could also contribute to stabilize the carbamic acid species probably through an intramolecular hydrogen bond upon complexation (Table 1, entry 11 vs. entry 3).^[9]

Cations of the ionic absorbents able to coordinate with solvents like PEG could thereby have influence on CO_2 capture. Indeed, of the cations tested (including potassium, lithium, tetrabutylammonium/phosphonium, DBUH⁺ (1,8-diazabicyclo[5.4.0]undec-7-enium), TBDH⁺ (1,5,7-triazabicyclo[4.4.0]dec-5-enium), and TMGH⁺ (1,1,3,3-tetrame-

thylguanidium), the sodium cation gave the best capacity (see Table S1 in the Supporting Information). The effect of the molecular weight of the PEG solvent was also investigated by using sodium *N*-isopropylglycinate (Table S2). PEG with a molecular weight deviating from 150 showed less favorable promotion, indicating that a suitable PEG chain length is required for coordination with sodium; PEG₁₅₀ monomethyl ether also showed lower capacity in comparison with PEG₁₅₀ possibly because of its weakened solvation power.

A further barrier to practical CCS would be high energy requirements for the desorption process. To our delight, the absorbed CO₂ in the present system was easily removed at temperatures as low as 40 °C by bubbling N₂ through the solution or at 90 °C in the absence of N₂. Since higher temperatures are required for CO₂ removal from the conventional amine-based absorption setup, this is an indication that our system proceeds by the carbamic acid pathway (Scheme 1 b). A negligible decrease in CO₂ capacity was observed after five consecutive absorption–desorption cycles (see Figure S1 in the Supporting Information).

To gain a deeper insight into the absorption mechanism involving the formation of a carbamic acid intermediate,^[13] we studied the amino acid salts by in situ FTIR spectroscopy under CO₂ pressure (Figure 1). The IR spectra of sodium *N*isopropylglycinate in PEG₁₅₀ before and after reaction with CO₂ are shown in Figure 1a.^[14] Firstly, the O–H and C–H stretching bands at 3319 and 2873 cm⁻¹, respectively, present



Figure 1. Results of in situ IR spectroscopy under CO_2 pressure. a) sodium N-isopropylglycinate in PEG₁₅₀ before and after CO_2 uptake at 25 °C; b) spectra of the absorption mixture with reaction time.

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no change after CO₂ uptake, indicating that PEG could be chemically inert during the process. Secondly, distinct bands corresponding to the ammonium cation between 2800-3000 cm⁻¹ and in the 2000–2800 cm⁻¹ region are not observed (new peak at 2338 cm⁻¹ corresponds to physically dissolved CO_2).^[15] Thirdly, since no peaks emerge at 1545 cm⁻¹ and 835 cm⁻¹, the formation of the carbamate and bicarbonate anions is excluded.^[7b] Finally, two characteristic peaks centered at 1644 and 1663 cm⁻¹ can be assigned to asymmetric (C=O) vibrations of the carboxylate anion and COOH moiety of the carbamic acid, respectively. Figure 1b explicitly shows the changes in the IR peaks with reaction time, as the weakening of the signal of carboxylate anion of sodium Nisopropylglycinate at 1596 cm⁻¹ is accompanied with the increase of the new peaks at 1644 and 1663 cm⁻¹. Furthermore, the FTIR spectrum of the isolated absorption product^[16] (Figure S3 in the Supporting Information) indicates that the N-H stretch at 3286 cm⁻¹ significantly weakens upon CO₂ uptake.

Subsequent NMR investigations were performed to get information about the formation of the carbamic acid product (Figure 2). In the ¹H NMR spectrum, the downfield shift of the N-CH (2, from $\delta = 2.81$ to 3.13 ppm) and N-CH₂ signals (3, from $\delta = 3.14$ to 3.31 ppm) could indicate that CO₂ is chemically bound to the nitrogen center (Figure 2 a,b). Simultaneously, the new peak at $\delta = 161.4$ ppm after CO₂ uptake would support the formation of the carbamic acid structure between the secondary amine and CO₂ (Figure 2e), since this chemical shift is close to previously reported values.^[9,13,17] In the ¹³C NMR spectrum, signals at $\delta = 62.0$, 71.3, and 73.5 ppm also indicate that PEG₁₅₀ does not interact chemically with CO₂ (Figure 2d,e). The purified product was then investigated by ¹H and ¹³C NMR spectroscopy (Figure 2 c,f). Only one additional carbonyl signal at $\delta =$ 161.5 ppm was detected which is identical to that for the crude product and in agreement with the formation of the carbamic acid.

DFT-calculated enthalpy changes for the present equimolar CO₂ capture also support formation of the carbamic acid product (Figure 3). Following the prevalent mechanism for the amine-based CO₂ absorption, the amino acid salt with PEG_{150} coordinated at the sodium cation (A) reacts with CO_2 at the secondary amine to form the carbamic acid (B), which is probably stabilized through an intramolecular hydrogen bond with the carboxylate anion,^[9] thus leading to enhanced CO₂ absorption capacity (Table 1, entry 3 vs. entry 11). This interaction was detected by in situ FTIR spectroscopy under CO₂ pressure: the C=O vibration of the carboxylate shifted to higher frequency upon introduction of CO₂ (Figure 1). Formation of the carbamic acid product **B** with a calculated enthalpy change of $-10.4 \text{ kcal mol}^{-1}$ should be thermodynamically favorable. In step II, B may further react with A to generate the ammonium carbamate (C) and a 2:1 stoichiometry would result accordingly. However, such a step is endothermic presumably because of the steric repulsion of the isopropyl substituent at the nitrogen center of A with the approaching **B**. On the other hand, the concerted path (III) for carbamate formation is also thermodynamically unfavorable. As a consequence, the proposed formation of the



Figure 2. ¹H and ¹³C NMR spectra (CD₃OD) of sodium *N*-isopropylglycinate in PEG₁₅₀ (a, d), the resultant mixture after CO₂ absorption (b, e), and the isolated absorption product (c, f).

carbamic acid is rational, thus leading to equimolar CO_2 capture. In contrast, external energy input would be required for the generation of the ammonium carbamate.

The high energy requirements of CO_2 desorption, compression, and transportation could be critical problems in current CCS processes. Meanwhile, the development of the catalytic transformation of CO_2 into value-added compounds is also confronted with problems related to energy input for CO_2 activation.^[4eg,18] Therefore, the challenge is to develop alternative protocols to integrate the energy input for both CCS and chemical transformation, hence circumventing the high energetic cost. We propose that the captured CO_2 in the form of the carbamic acid could be more reactive in lieu of free CO_2 , thus rather than desorption of CO_2 the subsequent



Figure 3. Enthalpy changes of reactions I, II, and III in ethanol, calculated by the M06-2X/6-311 + +G(d,p)//B3LYP/6-31 + G(d)/CPCM method. **A**: sodium *N*-isopropylglycinate coordinated with PEG₁₅₀; **B**: carbamic acid from CO₂ and one mole of **A**; **C**: ammonium carbamate from CO₂ and two moles of **A**. H: white, C: gray, N: blue, O: red, Na: violet. Bond lengths and distances in Å.

conversion would produce chemicals. The strategy for carbon capture and utilization (CCU) was validated by reacting the absorbent amino acid salt after CO_2 uptake (1 atm) with a substrate in the presence of a catalyst. Oxazolidinones can be synthesized in high yields from the reaction of the captured CO_2 with either aziridine or propargyl amine (Scheme 2).



Scheme 2. Oxazolidinone synthesis upon CO_2 absorption with sodium *N*-isopropylglycinate in PEG₁₅₀.

In summary, readily prepared sodium *N*-isopropylglycinate was found to be the best absorbent for the rapid and reversible capture of CO_2 at a stoichiometry of almost one molecule of CO_2 per amino group. This is the first example of steric-hindrance-controlled CO_2 absorption, thereby leading to equimolar CO_2 absorption and ready desorption. This process, which is assumed to proceed via the carbamic acid rather than the ammonium carbamate, was studied by NMR and in situ FTIR spectroscopy and computational calculations. Furthermore, the capture of CO_2 could simultaneously result in its activation, such that subsequent conversion into valuable compounds may be more favorable than the desorption process.

Received: July 7, 2012 Published online: October 8, 2012

Keywords: amino acids · carbamic acid · carbon dioxide fixation · catalysis · poly(ethylene glycol)

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for the amino acid salt after CO₂ uptake (Table 1, entry 3): $\delta = 18.5$, 46.8, 50.1, 161.1, 172.4 ppm. In addition, ¹³C NMR spectra are provided in the Supporting Information.

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