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Pyrrolizidines for Direct Air Capture and CO₂ Conversion

Jan M. Hanusch,^[a] Isabel P. Kerschgens,^[a] Florian Huber,^[a] Markus Neuburger^[b] and Karl Gademann*^[a]

Greenhouse gases such as CO₂ strongly contribute to the rising temperatures of our planet, but as long as our society is dependent on fossil fuels, this trend will even increase in the near future. Therefore, CO₂ capture and subsequent utilization constitute an approach for decarbonization and CO₂ mitigation, and for this purpose, amine scrubbing remains the industrially most established process. In this article, we describe the CO₂ capture-ability of pyrrolizidine-based diamines, a scaffold with remarkably good properties to fulfill this challenge. We observed fast equimolar CO₂-uptake, as well as high stability of these compounds during multiple capture and release-cycles. In addition, the amines could be utilized for direct air capture. Finally, we demonstrate the utility of the pyrrolizidine absorbents in the reduction of CO₂ and for the formation of oxazolidinones.

Global warming has been suggested to correlate with the rising CO₂ levels that have been observed over the last decades.^[1] Among many strategies proposed to counter this trend, CO₂ (*i.e.* carbon) capture and utilization (CCU) stands out from a chemical point of view.^[2] A number of chemical systems have been developed,^[2f] that allow for the sequestration of CO₂ from gas mixtures such as flue and combustion gas (5-15% CO₂)^[3] or even directly from air (400 ppm CO₂).^[4] However, a number of challenges remain for the design of efficient CO₂ capture agents: (1) a high affinity to CO₂ is required to allow for sequestering CO₂ at 400 ppm levels from the atmosphere; (2) the ability to desorb CO₂ for release and subsequent conversion with little energy; (3) the stability of the absorbent over repetitive cycles of absorption and desorption. Although some promising solid absorbents^[5] were recently developed, liquid amine absorbents^[6a] remain as the industrially most used agents for the reversible capture of CO₂ due to their low cost and convenient handling. Monoethanol amine (MEA)^[6b] constitutes the most established amine absorbent and is used for the capture of CO₂ from natural gas or industrial gas mixtures. The drawbacks of MEA include the high regeneration temperature and the significant decomposition^[7] during this process. In the context of our work on 7a-substituted pyrrolizidine

over conventional amines due to their arrangement in solution (Figure 1). Experimental support for this hypothesis was reported in the literature, for example in the natural product temuline by Trauner and co-workers.^[9]

For our studies on the CO₂ uptake performance we started with the industrial most common MEA (**1**) as a comparison,^[10] as well as the linear amine **2**. We measured the overall uptake capacity as well as a value for comparison of the kinetics. Therefore, we decided to use the t_{90%} value which represents the time until 90% of maximal saturation for each amine is reached, which allows deeper insight into the kinetic. Since we observed a significant and large difference in weight, gravimetric measurement was our method of choice to quantify the uptake capacity.^[11] To have a good gas/liquid contact area, we decided to use PEG₂₀₀ as a solvent. This solvent was already established in earlier CO₂ uptake studies^[12] and has only small CO₂ uptake capacity itself, as well as a high boiling point, mitigating the issue of solvent evaporation. Previous work in our group already gave access to amine **4**^[9] and in a first experiment both homologues **3** and **4** were used. Exposure to the uptake conditions remained rather unfruitful for both aniline derivatives. Additionally, both primary amines **5** and **6** were prepared and exposure to the same uptake conditions already showed equimolar uptake and a better t_{90%} value for amine **6** compared to the linear amine **2** was observed. Through hydroformylation and subsequent reduction both mono-methylated derivatives **7** and **8** were successfully synthesized.

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carboxamides^[8] we realized that the corresponding diamines reacted with CO₂ in a reversible manner (Figure 1). We hypothesized that aminopyrrolizidines have several advantages

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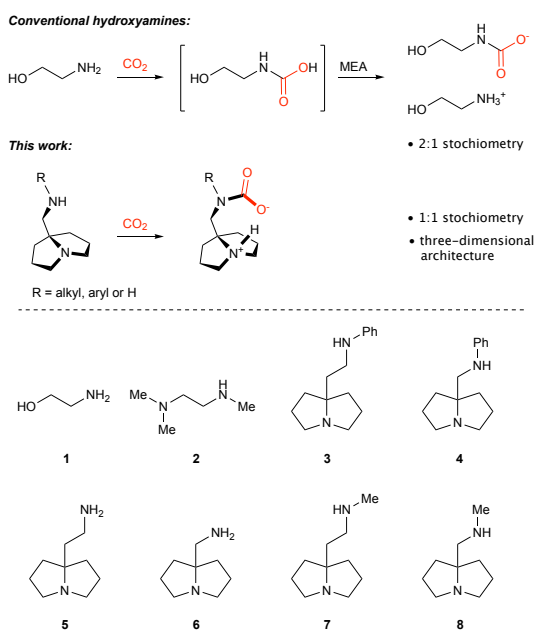


Figure 1. Comparison of conventional hydroxyamines to pyrrolidine-based diamines.

Both showed a similar uptake capacity than **5** and **6**, but we were very pleased, that amine **8** showed a fantastic $t_{90\%}$ value of only 28 min. (Table 1, Figure 2). This value was clearly better than for the linear amine **2**, which underlines the hypothesis, that the caged structure of pyrrolidine diamines has a positive influence on the performance of CO₂ capture and leads to a $t_{90\%}$ value three times faster than MEA (**1**). From the measured values, we could conclude that the distance between the two amine units does not have an impact on the uptake capacity, but correlates with the $t_{90\%}$ value (Figure 3). The 1,2-diamines probably form a more favoured transition state, which leads to the faster uptake ability of amines **6** and **8** compared to their higher homologues (Figure 2). The slightly overstoichiometric uptake could be explained by the formation of bicarbonate salt adducts.

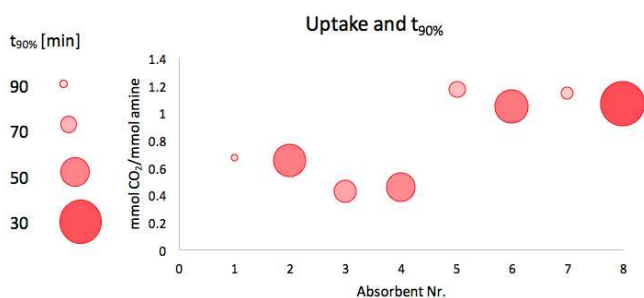


Figure 2. Uptake capacity and graphically illustrated $t_{90\%}$ values of the different absorbents **1-8** with pure CO₂.

Furthermore, all pKa values of the corresponding acids of the amines were determined and were close to the range of known absorbents.^[13] Nonetheless, a real correlation of the pKa values to the uptake capacity or the kinetic was not found. Next, we investigated the reversibility of absorption and desorption over several cycles and a longer time frame. Although the overall CO₂ uptake capacity of **8** was lower than for **7**, we decided to investigate the reversibility of the uptake with diamine **8** due to

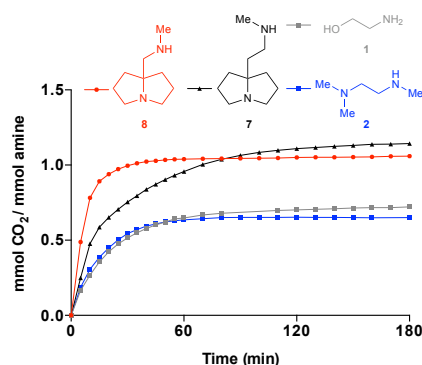


Figure 3. CO₂-absorption curves of pyrrolidine **7** & **8** in comparison to MEA (**1**) and linear diamine **2** with pure CO₂. All measurements include PEG₂₀₀ (12 mmol).

its great kinetic behaviour (Table 1, Figure 3). For the uptake, the sample was charged with CO₂ at 9 mL/min to about 90% of total capacity, to complete more absorption and desorption cycles in a shorter time frame. For the release, the sample was heated to 65 °C while charging the sample with N₂ until 20% capacity within 70 min.

Table 1. CO₂ absorption of pyrrolidine derivatives **3-8** and commercially available absorbents.^[a]

absorbent	pKa ^[b]	CO ₂ absorption ^[d]	$t_{90\%}$ [min] ^[f]
PEG ₂₀₀	-	0.08 ^[e]	-
1	9.6	0.67	87
2	10.0, 6.1	0.65	47
3	11.4	0.42	63
4	10.5 ^[c]	0.45	52
5	11.2, 8.4	1.17	73
6	10.7, 6.2	1.04	45
7	11.3, 8.6	1.14	80
8	10.6, 6.6	1.06	28

[a] Conditions: PEG₂₀₀ (12 mmol) and absorbent (3 mmol), 25 °C, pure CO₂ stream 9 mL/min, value after 180 min. [b] pKa was determined by titration of an aq. amine soln. (0.01M) with aq. soln. HCl (0.01M). [c] Amine was dissolved in MeOH. [d] Molar ratio of CO₂ per absorbent, absorption by PEG₂₀₀ is included. [e] CO₂ absorbed per 4 mmol of PEG₂₀₀. [f] Time until 90% saturation, values for 70% and 50% saturation are added in the SI.

As evident from Figure 5, the uptake and release showed excellent reversibility over 14 cycles. In addition, as other amine absorbents often display considerable decomposition,^[7] this data show that no decrease in uptake performance was observed, which underlines the hypothesis that no significant decomposition of the amine took place. In addition, we could demonstrate that the uptake also takes place at 50 °C and in pure water or the presence of water (see SI, quant. ¹³C-NMR analysis), documenting even higher capacity for water-containing gas streams and flue gas at elevated temperatures. In summary, the excellent stability, high capacity, excellent kinetics and good reversibility, showcase the excellent structural framework of caged diamines of type **8** for CO₂ absorption and release.

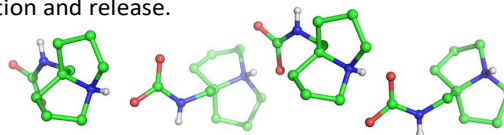


Figure 4: Single crystal X-ray structure of the carbamate adduct of pyrrolidine **6** (water molecules were omitted for clarity).

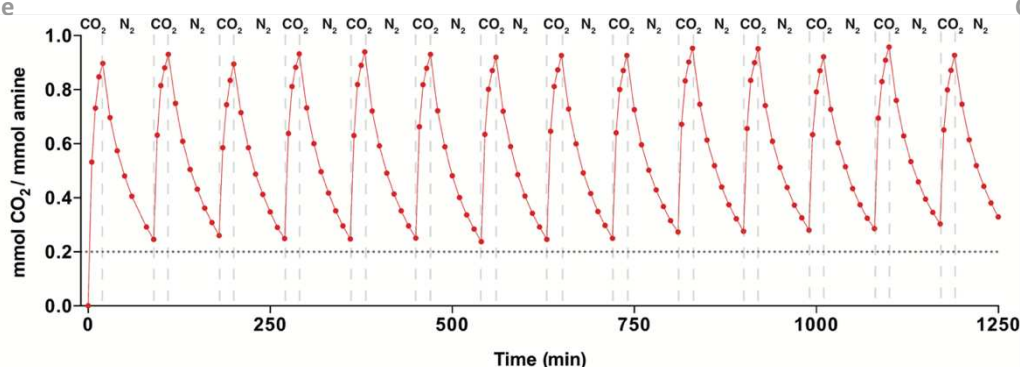


Figure 5: Absorption and desorption cycles of absorbent **8**. The uptake/release experiment was carried out over 9 days. For uptake, a pure CO₂ flow of 9 mL/min was applied (measurement every 5 min). After 20 min, the headspace was exchanged with N₂. For the release a N₂ flow of 9 mL/min was applied and the sample was placed in a 65 °C waterbath (measurement every 10 min).

Next we investigated the structural and mechanistic aspects of CO₂ fixation. Some amines turned into solids under neat exposure to CO₂ and it was possible to observe single X-ray structure analysis,^[14] which clearly showed the newly formed carbamate structure (Figure 4).

Interestingly, amines **3** and **4** never showed solid formation upon CO₂ exposure. Based on this observation, as well as pKa and NMR studies, we suggest that these two compounds do not form the carbamates but instead remain as the bicarbonate salt (see SI for discussion). Since a lot of amines interact well with pure CO₂, we wanted to demonstrate the power of the pyrrolizidine based diamines on more diluted gas mixture. We decided to use a 10% CO₂ gas stream, which is an average value

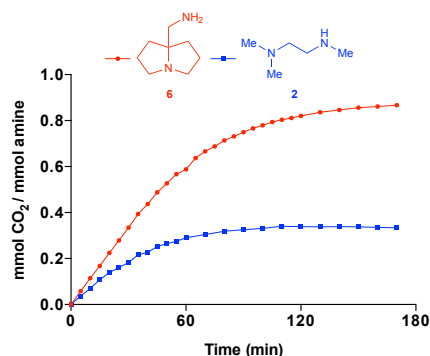


Figure 6. CO₂-absorption curve of pyrrolizidine **6** in PEG₂₀₀ with gas mixture CO₂ (10%) and N₂ (90%) compared to linear diamine **2**.

for flue gas (5-15% CO₂) and these low concentrations still depict a challenge for absorbents.^[2f, 4a, 15] Even though the structural parameters are similar, the significant higher overall uptake as well as the faster rate showcased again a big advantage of the caged diamine over the linear analogue **2** (Figure 6).

After good performance with pure CO₂ (Figure 3) as well as flue gas (Figure 6), the affinity to very low CO₂ concentrations in direct air capture (DAC, ~400 ppm CO₂) was investigated. Therefore, we treated pyrrolizidine **6** over 9 days with compressed air and the results are shown in Figure 7. A significantly higher weight increase over time was observed by using the absorbent compared to the blank measurement. Additionally, we analyzed the mixtures by NMR spectroscopy after treatment with compressed air (see SI), and the data clearly displayed the newly formed carbamate resonance at 166.35 ppm indicating the binding of CO₂. Furthermore, comparison of the NMR spectra with an oxidized sample

showed no oxidation of the absorbent (**S7**, SI). We found that the CO₂-uptake varies with the source of compressed air, which needs to be further investigated in larger scale experiments. Next, we investigated the performance of these diamines in the

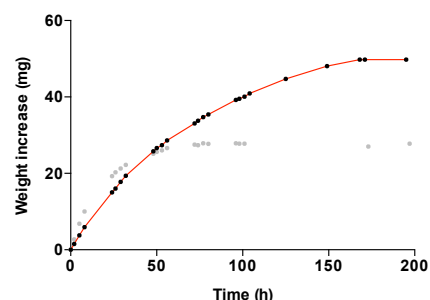
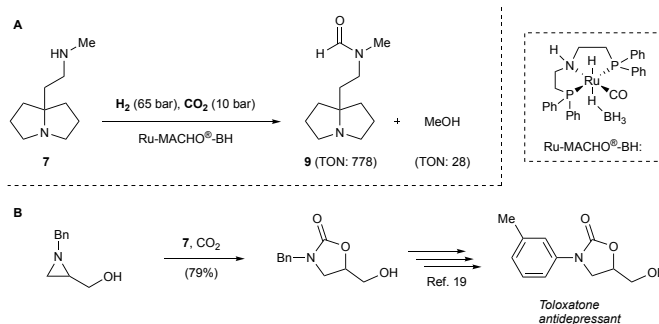


Figure 7: Direct air capture uptake curve of pyrrolizidine **6** and PEG₂₀₀ (black/red) compared to the blank measurement (grey). Conditions: compressed air (9 mL/min), 3 mmol of amine in 12 mmol PEG₂₀₀, blank: 12 mmol PEG₂₀₀.

realm of CO₂ conversion.^[16] In earlier studies, the groups of Sanford^[17] and Olah^[18] established the reduction of CO₂ to methanol using simple amines like dimethylamine and pentaethylenehexamine. Using Ru-MACHO[®]-BH as a catalyst, the 2-electron reduction of CO₂ to the corresponding formamide was achieved in a high turnover number (TON=778). Furthermore, the reaction also delivered methanol as the product of the 6-electron reduction (Scheme 1).

For a further application we investigated the use of pyrrolizidines for the transformation of aziridines into oxazolidinones. Due to various reports amines are known to act as catalysts for the capture and conversion of CO₂.^[2c, 15a, 19] However there are only few reports describing the catalyzed transformation of aziridines into oxazolidinones where either a high CO₂-pressure or a co-catalyst was required for the reaction.



Scheme 1: Conversion of CO₂ with pyrrolizidine. Conditions: **A** 3.08 mmol amine **7**, 120 μmol K₃PO₄, 2.39 μmol Ru-MACHO[®]-BH, 1.7 mL THF, 155 °C, 134 h; **B** 184 μmol aziridine **10**, 92.0 μmol amine, 0.9 mL DMSO, 1 atm CO₂, 160 °C, 15 h, isolated yield: 79%.

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Furthermore, substituted aziridines gave a 1:1 mixture of the two regioisomers.^[20] Here we could deploy pyrrolizidines as a CO₂-capturing source in the formal synthesis of the reversible monoamine oxidase A inhibitor *Toloxatone* (**12**, Scheme 1).^[21] Aziridine **10** could be obtained in two steps from methyl 2,3-propanoate in good yields.^[22] Deploying substoichiometric amounts of the pyrrolizidine **7**, we could incorporate CO₂ under opening of the aziridine leading to the desired oxazolidinone **11** in good yields. The other regioisomer could not be detected. The cyclic carbamate can be further transformed into *toloxatone* **12** following literature known deprotection of the benzyl group and a Cu catalyzed coupling.^[23]

Conclusions

In conclusion, pyrrolizidine based diamines showed reversible and high performance uptake of CO₂, with excellent stability and reversibility over multiple cycles. In addition, the bifunctional absorbents were able to capture CO₂ both in neat form and in solution. The resulting solid from CO₂ capture of the neat compound was analyzed by X-ray crystallography and provided a structural insight. We also showed that the amines can be utilized for conversion of CO₂ to the corresponding formamide, methanol and for the synthesis of oxazolidinones.

Conflicts of interest

The authors declare no conflicts of interest.

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