Sustainable Chemistry

Carbon Dioxide Capture and Use: Organic Synthesis Using Carbon Dioxide from Exhaust Gas**

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Dedicated to Professor Robert H. Grubbs

Abstract: A carbon capture and use (CCU) strategy was applied to organic synthesis. Carbon dioxide (CO_2) captured directly from exhaust gas was used for organic transformations as efficiently as hyper-pure CO_2 gas from a commercial source, even for highly air- and moisture-sensitive reactions. The CO_2 capturing aqueous ethanolamine solution could be recycled continuously without any diminished reaction efficiency.

Recycling carbon dioxide (CO_2) as a renewable and environment-friendly source of carbon is one of the most attractive solutions to reduce our dependence on petrochemicals. One of the main approaches to recycle CO_2 is its capture and use (CCU);[1] this approach has the potential to afford value-added products from the sustainable C_1 feedstock and to make large-scale cuts in atmospheric CO_2 emissions by capturing anthropogenic CO_2 without restructuring or closing the industrial plants.

Currently, amine scrubbing technology is used for capturing CO_2 in industry,[2] while the development of advanced CO_2 capture materials such as ionic liquids and metal–organic framework materials is underway.[3] In the amine-based CO_2 capture process, alkanolamines selectively react with CO_2 in flue gas to form the corresponding carbamates (Figure 1).[4] The alkanolamines can be recovered by stripping CO_2 with water vapor at 100–120 °C and recycled back to the beginning of the process. After the water is condensed from the stripper vapor, the CO_2 is compressed to 100–150 bar. The condensed CO_2 is then transported using pipeline or ship for geologic sequestration, and only a small portion of it is used as a C_1 source for chemical synthesis.[5] A high cost is paid for the transportation and sequestration.

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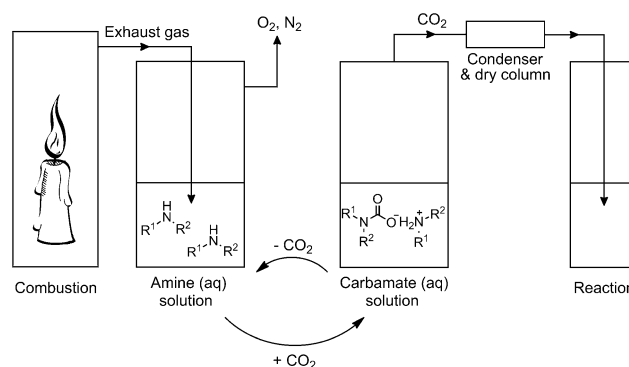

Figure 1. Carbon dioxide capture and use for organic synthesis.

Therefore, it is highly desirable to use the environment-friendly raw material, CO_2, as a C1 source for synthesizing fine chemicals. Urea has already been synthesized on an industrial scale using CO_2.[6] Moreover, catalytic syntheses of polycarbonates[7] and cyclic carbonates[8] have recently been commercially used. Significant amounts of academic research have been conducted to transform CO_2 into fine chemicals.[9,10] Inspired by the overall CCU concept, we envisioned that the CO_2 from exhaust gas rather than commercial CO_2 gas can be used for usual organic syntheses. Herein, we report an unprecedented strategy for using CO_2 that is captured from combustion sources for organic syntheses (Figure 1).

We devised our strategy as follows: 1) selective capturing of CO_2 generated from fossil fuel combustion using an alkanolamine solution[11] and then 2) conduct organic reactions with CO_2 released from the captured material (Figure 1). The alkanolamine solution used in the process can be recycled for subsequent capture and release processes. To test this idea, previously reported silver-catalyzed carboxylation of alkynes[12] was chosen as the model reaction to confirm if the amount and purity of CO_2 released from the captured materials are sufficient to carry out an organic reaction (Table 1).[13] When hyper-pure CO_2 (> 99.999 %) obtained from a commercial supplier was directly applied to the reaction mixture under atmospheric pressure, the carboxylation of acetylene afforded the corresponding product in 83 % yield (Table 1, entry 1).[12]

Several alkanolamine solutions either in DMF or water (e.g., 7 molality (m), about 30 % ethanolamine (MEA) by weight, the most used concentration and CO_2 capture material in industry, respectively) have been tested as CO_2 capture and release materials.[11] To optimize the reaction conditions, hyper-pure CO_2 gas was introduced into the alkanolamine solution for 15 min, and the saturated CO_2

Table 1: Alkyne carboxylation reaction to test efficiencies of CO_2 capturing solutions.[a]

Entry	Amine[b]	Solvent	Volume [mL][c]	Yields[d]
1[e]	Pure CO_2 (>99.999%)	–	–	83%
2	HO–NH₂	H_2O	25	82%
3	HO–NH₂	H_2O	5	67%
4	HO–NH₂	DMF	5	73%
5	HO–N(H)–OH	H_2O	5	73%
6	HO–N(H)–OH	DMF	5	59%
7	(OH)–N(H)–(OH)	H_2O	5	8%
8	(OH)–N(H)–(OH)	DMF	5	67%
9	HO–N(CH₃)–OH	H_2O	5	19%
10	H₂N–(C)–OH	H_2O	5	69%

[a] Reaction conditions: phenylacetylene (1.0 mmol, 1.0 equiv), AgI (2.5 mol%), Cs_2CO_3 (1.5 equiv), CO_2 (ambient pressure) from an amine solution, DMF (10 mL), 25°C, 16 h. [b] Pure CO_2 was captured by the amine solution for 15 minutes. [c] Volume of solvent, and molality of amine solutions: 7 m. [d] Yield of isolated products. [e] The reaction was performed with hyper-pure CO_2 gas.

solution was used as the CO_2 source for the model reactions. Most of the tested alkanolamine solutions were suitable to be used as CO_2 capture and release material (Table 1). Both DMF and water worked well as the solvent for MEA (Table 1, entries 2–4).[2] For our reaction scale (1 mmol), about 35 mL of aqueous MEA solution (7 m, 25 mL of the solvent) was enough to show activity comparable to that obtained using commercial hyper-pure CO_2 gas (Table 1, entries 1 and 2). In the case of diethanolamine, a secondary amine, the reaction afforded better yield of the product in water than in DMF (Table 1, entries 5 and 6). The use of diisopropanolamine afforded a poor yield (8%) of the product in water; however, a moderate yield (67%) was obtained in DMF (Table 1, entries 7 and 8).[14] Because tertiary N-methyldiethanolamine (no acidic H present) cannot react with CO_2, its solution in DMF could not be used to capture CO_2 and no reaction occurred.[15] However, its aqueous solution afforded 19% yield of the product (Table 1, entry 9). This is because N-methyldiethanolamine acts as a base and promotes CO_2 hydrolysis to afford carbonates that can produce CO_2 upon heating.[15] Sterically hindered 2-amino-2-methyl-1-propanol that was used to prevent degradation at high temperature afforded the product in good yields (69%, Table 1, entry 10).[15] Among the alkanolamine solutions tested, the aqueous MEA solution was chosen as the optimum CO_2-capturing solution because of excellent CO_2 capture and

release capability and low costs, which also account for it being the most popularly used in industry.[16]

Encouraged by the initial results, the strategy to use CO_2 from exhaust gas was further applied to the carboxylation of various alkynes (Table 2).[12] A burning candle, a mixture of C_{20}–C_{40} hydrocarbons, was selected as the combustion source. An aqueous MEA solution (7 m, 25 mL of H_2O) in a reaction tube was chosen to capture CO_2 from the combustion source and then release CO_2 for the target reaction. The recycled solution was used for all the experiments listed in Tables 2 and 4. Photographs of the reaction set up following the design in Figure 1 are presented in the Supporting Information (Figures 1S and 2S in the Supporting Information). Although some soot was produced due to incomplete combustion, to our delight, the carboxylation reactions with released CO_2, which was captured by the MEA solution from the combus-

Table 2: Alkyne carboxylation using CO_2 from combustion.[a]

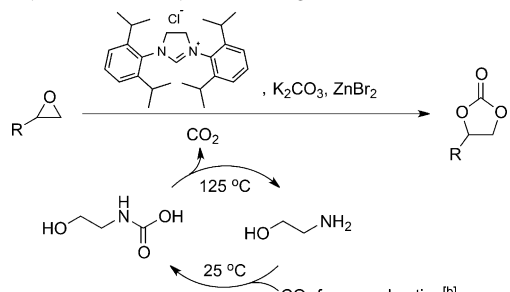| Entry	Substrates	Recycle times	Yields [%]
1		1	82
2		55	80
3[c]	⬡—≡—CO_2H	3	81
4[d]		–	0
5[e]		–	39
6	Me—⬡—≡—CO_2H	2	84
7	F—⬡—≡—CO_2H	24	78
8	O—⬡—≡—CO_2H	26	80
9	tBu—⬡—≡—CO_2H	14	88
10[f]	⬡—CH₂—≡—CO_2H	32	81
11	⬡—O—CH₂—≡—CO_2H	30	85
12	HO—⬡—≡—CO_2H	21	90
13[f]	Cl—⬡—≡—CO_2H	20	89
14[f]	⬠—≡—CO_2H	18	67
15[f]	⬡—CH₂—≡—CO_2H	12	65

[a] Reaction conditions: alkynes (1.0 mmol, 1.0 equiv), AgI (2.5 mol%), Cs_2CO_3 (1.5 equiv), CO_2 (ambient pressure) from an aqueous MEA solution (7 m, 25 mL of H_2O), DMF (10 mL), 25°C, 16 h. [b] A candle was burned for 3 h, and the CO_2 from the exhaust gas was captured in the MEA solution. [c] CO_2 was generated by methanol combustion. [d] Exhaust gas was directly introduced to the reaction mixture for 7 h. [e] Dry ice was directly added to the reaction mixture. [f] 50°C, 24 h.

tion of the candle, were as efficient as that with hyper-pure CO_2 gas (80–82% yields, Table 2, entries 1–3). Furthermore, even after recycling the MEA solution 55 times, the reaction yield did not reduce significantly (80% yield, Table 2, entry 2). When another combustion source, methanol, was used for CO_2 generation, the reaction efficiency was not affected either (81% yield, Table 2, entry 3). However, no reaction occurred when the exhaust gas from the combustion of candle was directly introduced into the reaction medium (Table 2, entry 4), which showed that it was essential to use the MEA solution to increase the CO_2 concentration and purity of the combustion gas. Dry ice, a general source of CO_2 in organic chemistry, was directly introduced into the reaction; however, the yield (39%) was low, presumably due to the reaction being sensitive to air and water (Table 2, entry 5). The substrate scope was expanded using the recycled aqueous MEA solution (Table 2). All the reactions were run twice, and proceeded smoothly exhibiting comparable reaction yields with previously reported studies using hyper-pure CO_2 gas.[12] The reaction yields were consistent regardless of the number of times that the aqueous MEA solution was recycled.

Next, CO_2 was incorporated into epoxides to form cyclic carbonates to check for the applicability of this method to other reactions.[8] There is an increasing demand for cyclic carbonates in both industry and academia.[8,17] Carbonates are used as monomers to synthesize polycarbonates and polyurethanes.[7] Furthermore, the hydrogenation of cyclic carbonates is a promising route to convert CO_2 to methanol, an excellent alternative fuel.[18] Therefore, the syntheses of carbonates using CO_2 gas from combustion sources are an attractive route for carbon recycling. The incorporation of CO_2 into epoxides to synthesize carbonates is usually performed at pressures higher than 1 atm.[8] Very recently, Shi and co-workers reported a carbonate synthesis under atmospheric pressure using commercially available N-heterocyclic carbene (NHC) and $ZnBr_2$ as the catalyst.[19] We applied our strategy to evaluate this reaction. Although the reactions involving NHC are usually air and moisture sensitive, all the product were obtained in excellent yields using the released CO_2 that was captured by the MEA solution from the combustion source (90–93%, Table 3). Therefore, the quality of CO_2 captured using the MEA solution was sufficient to conduct even air and moisture sensitive reactions using NHC-based transition metal catalysts.

Finally, we applied our strategy to one of the most widely used organic reactions, Grignard reaction.[20] The reaction of Grignard reagents with CO_2 using dry ice is a well-known synthetic route to obtain carboxylic acids. We conducted Grignard reactions to confirm the quality of CO_2 captured using the recycled aqueous MEA solution that had been used for alkyne carboxylation. Grignard reagents are very sensitive to moisture, as it causes protonation, and to O_2 in air, as it forms peroxides.[20] Therefore, it would be good to verify if this strategy can be applied to highly moisture and oxygen sensitive reactions. The incorporation of CO_2 into phenyl magnesium bromide using our set-up afforded benzoic acid in excellent yield (98% yield, Table 4, entry 1), which was

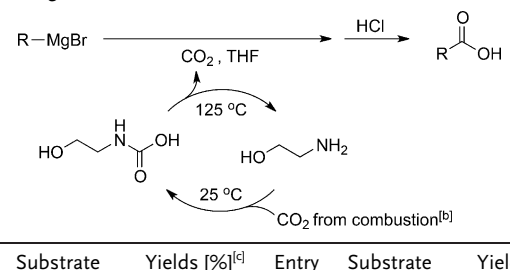***Table 3:*** Cyclic carbonate synthesis using CO_2 from combustion.[a]

Entry	Substrate	Yields [%][c]	Entry	Substrate	Yields [%][c]
1	(Ph carbonate)	90	3	(nBu carbonate)	93
2	(CH₂Ph carbonate)	91%	4	(CH₂Cl carbonate)	92

[a] Reaction conditions: epoxides (2.0 mmol 1.0 equiv), $ZnBr_2$ (2 mol%), K_2CO_3 (2 mol%), 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride (2 mol%), CO_2 (ambient pressure) from the captured material, DMSO (1 mL), 24 h, 80 °C. [b] A candle was burned for 5 h, and the CO_2 from the exhaust gas was captured in the MEA (aq) solution (70 mL, 7 m). [c] Yield of isolated products.

comparable to that of the reaction with dry ice (96%, Table 4, entry 2). The reaction could also be applied to other Grignard reagents performing carboxylations in high yields (89–99%, Table 4, entries 3–4). Notably, the use of 54-times-recycled MEA solution did not diminish the reaction efficiency (Table 4, entry 4).

In conclusion, an unprecedented organic synthesis strategy using CO_2 from exhaust gas was demonstrated. We have validated that the CO_2 generated from several combustion sources could be used in organic syntheses as efficiently as

Table 4: Grignard reaction with CO_2 from combustion.[a]

Entry	Substrate	Yields [%][c]	Entry	Substrate	Yields [%][c]
1	(benzoic acid)	98	3	(heptanoic acid)	89
2[d]	(benzoic acid)	96	4	(cyclohexanecarboxylic acid)	99

[a] Reaction conditions: Grignard reagents (1.0 mmol), THF (1 mL), CO_2 (ambient pressure) from the recycled captured material, 25 °C, 1 h. [b] A candle was burned for 3 h, and the CO_2 from the exhaust gas was captured in the aqueous MEA solution (7 m, 25 mL of H_2O). [c] Yield of isolated products. [d] Dry ice was directly added into the reaction tube as the CO_2 source.

hyper-pure CO_2 gas with $> 99.999\%$ purity from a commercial source. More importantly, the CO_2-capturing aqueous MEA solution could be recycled continuously without any decrease in the CO_2 capture and release efficiency. Furthermore, no difficulty was encountered in performing air and moisture sensitive reactions. Thus, in addition to demonstrating a model for CO_2 gas capture and use from combustion sources in fine chemical syntheses, we hope that our strategy could be used for carrying out organic reactions requiring CO_2 without using high-purity CO_2 gas and related equipment in an ordinary organic synthesis laboratory.

Experimental Section

General procedure of CO_2 capture and use from exhaust gas: MEA (10 mL, 166 mmol) and distilled water (25 mL) were placed in a Schlenk flask. To capture CO_2, the exhaust gas from the combustion of a candle was bubbled through the MEA solution for 3 h at room temperature. The CO_2-saturated solution could be stored at room temperature for more than a week and used when needed. The flask with the solution was connected to a reflux condenser. The top end of the reflux condenser was connected to a dry column linked to a bubbler. The MEA solution was heated to $125\,°C$ for 10–15 minutes to purge the set up with CO_2. Next, the bubbler was replaced with a gas line with a needle in the end. The target organic reaction (1 mmol scale) was set up separately in a Schlenk flask under inert conditions. The line from the captured CO_2 solution and the vent line with a bubbler were introduced into the target reaction flask while CO_2 evolution continued. The reaction flask was purged with CO_2 gas from the MEA solution for 5 minutes. Next, the vent line was exchanged with a balloon. CO_2 was captured in the balloon for 10–25 minutes until no more CO_2 evolved from the captured material. Next, the line from the CO_2 source was closed, and the reaction flask was isolated. The reaction continued under closed conditions with the equipped CO_2 balloon (see Figures 1S and 2S).

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