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Authors: Xiao-Fang Liu, Xiao-Ya Li, Chang Qiao, Hong-Chen Fu, and Liang-Nian He

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Betaine Catalysis for Hierarchical Reduction of CO₂ with Amine and Hydrosilane to Formamide, Aminal and Methylamine

Xiao-Fang Liu^a, Xiao-Ya Li^a, Chang Qiao^a, Hong-Chen Fu^a, Liang-Nian He^{*a,b}

Abstract: An efficient, sustainable organocatalyst i.e. glycine betaine was developed for reductive functionalization of CO₂ with amines and diphenylsilane. Methylamines and formamides could respectively be obtained with high yield via tuning CO2 pressure and reaction temperature. Betaine catalysis was efficient for the formation of formamide at 10 bar CO2 and 50 °C. Exclusively yielding methylamines from various amines with atmospheric pressure of CO2 was attained at 70 °C. Based on identification of the key intermediate i.e. aminal, an alternative mechanism for methylation involving the C⁰ silyl acetal and aminal was proposed. Furthermore, reducing CO₂ amount to approx. 1 equiv. afforded aminal with high yield and selectivity. Therefore, betaine catalysis in this study afforded the products with diversified energy content i.e. formamide, aminal and methylamine respectively through hierarchical 2-, 4- and 6-electron reduction of CO2 coupled with C-N bond formation for the first time.

In recent years, CO₂ has been already employed as a sustainable C₁ building block in organic synthesis.^[1] Among these, reductive functionalization of CO2 with amines and reductant, which combines both reduction of CO₂ and C-N bond construction and is illustrated using the so called "diagonal approach" by Cantat et al^[2], to produce versatile chemicals and energy-storage materials i.e. formamides, aminals and methylamines that are usually from petroleum feedstocks^[3] would be appealing and promising as shown in Scheme 1.^[4] In this context, metal-based catalytic systems including Ru,^[5] Fe,^[6] Cu,^[7] Zn,^[8] Ni^[9] and Cs^[10] have been developed. On the other hand, a number of organocatalysts, such as TBD (1,5,7triazabicyclo[4.4.0]dec-5-ene),^[2] NHCs (N-heterocyclic carbenes),[11] liquids)^[12] ILs (ionic as well as proazaphosphatrane superbases, [13] B(C₆F₅)₃^[14] and TBAF (tetrabutylammonium fluoride)^[15] have also shown high activity to afford formamides and/or methylamines.^[16] Notably, the carbon oxidation state in formyl of formamides and methyl of methylamines is +II and -II respectively, and the formation of C⁰ species (i.e. formaldehyde, aminal) from CO₂ remains a challenge. This may be because reduction of the C⁰ species to C^{-II} species (methanol, methylamine) is more rapid than reduction of formate derivatives (i.e. formic acid, formamide) to C⁰ species, which renders the C⁰ species elusive to be trapped and isolated.^[17] "As a consequence, only a few reports have

[a]	Xiao-Fang Liu, Xiao-Ya Li, Chang Qiao, Hong-Chen Fu, Prof.
	Dr, Liang-Nian He
	State Key Laboratory and Institute of Elemento-organic
	Chemistry, College of Chemistry
	Nankai University, Tianjin 300071 (China)
	E-mail: heln@nankai.edu.cn
[b]	Prof. Dr. LN. He
	Collaborative Innovation Center of Chemical Science and
	Engineering
	Nankai University, Tianjin 300071 (P.R. China)
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realized the reduction of CO₂ to formaldehyde^[18] Furthermore, few examples for combining reduction of CO₂ into the C⁰ function (i.e. methylene) with formation of new C–N, C–O or C–C bonds have ever been uncovered.^[17,19,20] For instance, Cantat *et al.* for the first time described the four-electron reduction of CO₂ with amines and hydrosilane to access aminals in 2015.^[17] Other reports for CO₂ reduction to C⁰ oxidation state coupled with formation of new bonds also include hydroformylation of olefins with CO₂ and carbonylative coupling with CO₂ via CO pathway.^[21]^w Hitherto, the hierarchical reduction of CO₂ with amine and hydrosilane to access formamides, aminal and methylamines remains unknown.^[22]



 $\label{eq:scheme-1} \begin{array}{l} \mbox{Scheme-1}. \ \mbox{Reductive functionalization of } CO_2 \ \mbox{with amine to afford formamide, } \\ \mbox{aminal and methylamine} \end{array}$

To resolve hierarchical reduction of CO₂, the selection of well-balanced catalyst that could subtly control the kinetics of CO₂ reduction is crucial.^[17] Betaine is known as an inner salt with onium cation and with negatively charged moiety e.g. a carboxylate anion, which could interact with silicon atom of hydrosilane, thereby generating the penta- or hex-coordinated silicon species and thus resulting in enhanced hydride donating ability.^[21] With reasonable interaction towards hydrosilane, betaine catalysis may balance the reactivity of CO₂ reduction and allow the C^{+II}, C⁰ and C^{-II} species to be stabilized selectively, whereby reaching hierarchical reduction of CO₂.

Herein, we would like to report glycine betaine (GB, 1carboxy-*N*,*N*,*N*-trimethylmethanaminium inner salt) as an excellent and sustainable organocatalyst for reductive functionalization of CO₂ with various amines and diphenylsilane. Selectively yielding methylamines and formamides, respectively, could be achieved by switching CO₂ pressure. Particularly, the reductive reaction could terminate selectively at the formaldehyde level i.e. aminal through subtly regulating CO₂ amount. As a whole, this protocol represents the first example for selective 2-, 4- and 6-electron reduction of CO₂ with amine and hydrosilane to products with various energy content i.e. formamide, aminal and methylamine, respectively.

For our initial investigation, the reductive functionalization of CO₂ with *N*-methylaniline (**1a**) in the presence of diphenylsilane as reductant was chosen as a benchmark reaction (Table 1). No product was detected without any catalyst (entry 1, Table 1), and betaine hydrochloride GB•HCI bearing proton at the oxygen atom of carboxylate showed no catalytic activity neither (entry 2). Excitingly, quantitative yield of methylation product i.e. *N*,*N*-dimethylaniline **1c** was obtained by employing GB as the catalyst (entry 3). Those results hint that free oxygen-nucleophilic species play a vital role in promoting the reaction. In

other words, because carboxylate is presumably able to activate CO₂ molecule as well as diphenylsilane via interaction of oxygen of betaine and silicon of hydrosilane to form the hypervalent silicon species, thus improving reducibility of hydrosilane.^[23] Further control experiments showed that carboxylate salts with ammonium cation work smoothly and the cation (e.g. ammonium group) tunes the catalytic activity via adjusting the nucleophilicity of carboxylate anion (Table S1, SI). Without CO₂, the reaction did not occur at all (entry 4), suggesting CO₂ is indispensable for this methylation. Furthermore, halving the catalyst loading did not influence on **1c** yield (entry 5); while decreasing the amount of diphenylsilane, **1c** yield declined to some extent (entry 6).

Interestingly, a considerable amount of N-methylformanilide 1b coupled with 1c was formed at relatively low temperature e.g. 50 °C (entry 7). The similar trend that low temperature favors for the formylation was also observed in the TBAF and Cs_2CO_3 catalysis.^[10a, 15] However, further decreasing temperature to 30 °C just gave a trace amount of 1b (entry 8). On the other hand, increasing CO₂ pressure to 10 bar, quantitative yield of 1b could be achieved (entry 9). This is because high CO₂ pressure represents high CO₂ concentration and large excess CO₂ would consume diphenylsilane, depressing further reduction and causing the reaction to terminate at N-formylation step. Even halving the amount of diphenylsilane, a 92% yield of 1b could still be attained (entry 10). Therefore, selective reductive functionalization of CO2 with amine to formamide and methylamine respectively was realized through switching the temperature and CO₂ pressure. The effects of different hydrosilanes were examined, demonstrating the priority of diphenylsilane for this reaction (Table S2).

With the optimal conditions in hand, we evaluated the scope of this newly-developed GB-catalyzed *N*-methylation protocol as shown in Scheme 2. A variety of secondary aromatic amines were smoothly methylated with good to excellent yields (**1c-10c**). Remarkably, excellent functional-group tolerance was observed for alkynyl (**5c**), ester (**6c**), alkenyl (**8c**) and hydroxyl (**10c**) group. In addition, secondary aliphatic amines showed moderate reactivity for methylation (**11c-12c**). Primary amines also were successfully methylated to furnish the corresponding *N*,*N*dimethylamines with moderate to good yield by doubling the amount of diphenylsilane and reaction time (**13c-18c**).

Furthermore, we explored the utility of the formylation of amines with CO_2 using GB as an organocatalyst (Scheme 2). Secondary aromatic amines with both electron-donating and electron-withdrawing substituent on the phenyl ring were suitable for this formylation, providing the corresponding formamide in 62–96% yields (**1b-4b**, **8b** and **19b**). It is worth mentioning that alkenyl (**8b**) and carbonyl (**19b**) groups were well tolerated in this catalytic system, demonstrating nice functional group compatibility. Aliphatic amines showed better activity than aromatic counterparts (**11b-12b**, **20b** *vs*. **1b-4b**), probably being ascribed to the stronger nucleophilicity. Additionally, primary amines behaved in a similar fashion to secondary amines, forming mono-formylated products (**13b-17b**).

Several control experiments were performed to explore possible intermediate in *N*-methylation reaction as depicted in SI. The *N*-methylation delivered methylamine **1c** coupled with trace

Ph	H N _{CH3} + CO ₂	+ hydrosil	ane —	GB) CHO CH₃ CHO CH₃ Ph ⁻ N-CH₃ ⁺ Ph ⁻ N-CH₃		
	1a		CH ₃ CN	1ь		1c
Entry	Catalyst	T/	P(CO ₂)	Conv. of	Yield of	Yield of
		°C	/atm	1a/% ^[b]	1b/% ^[b]	1c /% ^[b]
1	-	70	1	0	0	0
2	GB• HCI	70	1	trace	trace	trace
3	GB	70	1	>99	trace	98 (95) ^[g]
4 ^[c]	GB	70	0	0	0	0
5 ^[d]	GB	70	1	>99	trace	96 (91) ^[g]
6 ^[e]	GB	70	1	73	trace	72
7	GB	50	1	80	16	63
8	GB	30	1	trace	trace	trace
9	GB	50	10	98	96	trace
10 ^[f]	GB	50	10	94	92	trace

[a] Conditions: 1a (0.25 mmol, 27 μ L), GB (3.0 mg, 10 mol%), diphenylsilane (1 mmol, 186 μ L), CH₃CN (2 mL), 12 h. [b] Determined by GC using 1,3,5-trimethyoxybenzene as an internal standard. [c] N₂ balloon. [d] GB (1.5 mg, 5 mol%). [e] Diphenylsilane (0.75 mmol, 140 μ L). [f] Diphenylsilane (0.50 mmol, 93 μ L) and reaction time 18 h. [g] Isolated yield.

of formamide 1b (Figure S1), suggesting that formamide may serve as the active intermediate. However, formamide 1b as substrate was unable to give the methylated product 1c at all under otherwise identical conditions, which may exclude the possibility of formamide as the intermediate (eqn. 1, SI). On the other hand, urea 1d, which has ever been proposed as an intermediate in the Ru-catalyzed methylation of amine with CO2 and hydrosilane,^[5a] could not deliver **1c** neither (eqn. 2, SI). Furthermore, CO₂ could be reduced by diphenylsilane to diphenyldimethoxysilane (methanol level) under the identical conditions (SI), thus diphenyldimethoxysilane was examined as possible intermediate. However, methylamine 1c could not be obtained neither (eqn. 3, SI). These control experiments illustrate that three pathways for N-methylation involving formamide, urea and methanol, respectively do not work in this betaine catalysis.

To gain insight into mechanism of *N*-methylation, the dependence of reaction time over catalytic performance was further studied, and the results were given in Figure S1. A certain deviation appears between conversion of **1a** and total yield of **1b** and **1c** from 4 h to 6 h. The formation of silyl formate, acetal and methoxide (reductive products of CO_2 in the presence of diphenylsilane) as well as formamide **1b**, methylamine **1c** and *N*,*N'*-dimethyl-*N*,*N'*-diphenylmethanediamine **1e** (products of reductive functionalization of CO_2 with amine and hydrosilane) within 4-6 h could be confirmed by GC-MS (SI). Among those reactive species, the aminal **1e** was detected with 31% NMR

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yield in 4 h and almost vanished in 6 h, implying **1e** may be the intermediate. Indeed, the aminal **1e** was successfully isolated in this study,^[24] and further reacted with diphenlysilane under identical conditions afford a quantitative yield of **1c** (Scheme S4). These results support that the aminal is the feasible intermediates. In this context, Cantat *et al.* recently reported that the aminal was obtained through condensation between amine and C⁰ silyl acetal^[17] which has been detected in this GB-catalyzed reaction. Therefore, it can be concluded that this reaction goes through the C⁰ silyl acetal and aminal pathway.

Such results stimulated us to explore if the reaction could terminate at aminal i.e. C⁰ level. Therefore, further condition exploration was conducted as shown in Table 2. Temperature screening showed that 50 °C is optimal (entries 1-3, Table 2). Increasing the amount of CO₂ to approx. 2 equiv. relative to the amine led to a sharp drop in the yield of N,N'-dimethyl-N,N'diphenylmethanediamine 1e (entry 2 vs 4), which implies the amount of CO₂ is crucial in selectively obtaining aminal. This may be because inadequate CO₂ suppresses further reduction of aminal to methylamine. Halving dosage of GB did not influence on the yield of 1e (entry 2 vs 5). As such, employing phenylsilane as reductant delivered similar results (entry 2 vs 6). The reductive functionalization of CO₂ with amines to aminal was explored tentatively. Secondary aromatic amines N-methylp-toluidine 3a and 4-chloro-N-methylaniline 4a as well as heterocyclic compounds 21a worked well to afford corresponding aminals 3e, 4e, 21e (Scheme 2).

 Table 2. Condition exploration for reductive functionalization of CO_2 with N-methylaniline 1a to N,N'-dimethyl-N,N'-diphenylmethanediamine 1e

						All and a second s
Entry	T/⁰C	CO ₂	Conv. of	Yield of	Yield of	Yield of
		equiv	1a /% ^[b]	1b /% ^[b]	1 c /% ^[b]	1e /% ^[b]
1	30	1	trace	trace	trace	trace
2	50	1	99	trace	trace	93
3	70	1	61	trace	trace	59
4	50	2	65	9	19	37
5 ^[c]	50	1	99	trace	trace	93 (85) ^[e]
6 ^[d]	50	1	92	trace	4	87

[a] Condition: **1a** (1 mmol, 108 μ L), GB (11.8 mg, 10 mol%), Ph₂SiH₂ (6 mmol Si-H), CO₂ (approx. 1 mmol, closed), CH₃CN (2 mL). [b] Determined by ¹H NMR using 1,3,5-trimethyoxybenzene as an internal standard. [c] GB (5.9 mg, 5 mol%). [d] PhSiH₃ (Si-H 6 mmol). [e] Isolated yield.

On the basis of the above results and previous reports,^[4b] a possible reaction pathway for the present GB-catalyzed reductive functionalization of CO₂ with amine was proposed as depicted in Scheme 3. Employing atmospheric pressure CO₂, methylamine could be acquired exclusively. GB initially interacts with diphenylsilane through nucleophilic oxygen of GB and silicon of diphenylsilane, forming the hypervalent silicon species I bearing active hydride, which is also supported by DFT calculation.^[25] Subsequent hydride transfer from I to CO₂ delivers the silyl formate II, which goes through further reduction to give the C⁰ silyl acetal III. Then condensation between III and

the amine affords the aminal VI. Finally, VI is reduced to the methylated product VII in the presence of GB and diphenylsilane.



By raising CO₂ pressure and lowering reaction temperature, the formylated product V can be obtained with high yield and selectivity. Nucleophilic attack of the amine towards II delivers the formamide V. This is because excess CO₂ exhausts diphenylsilane to afford the silyl formate II, which is unable to go through further reduction without reductant. In addition, further reduction of CO₂ to the silyl acetal III may require high energy input compared with the reduction to the silyl formate II, and lower temperature thus disfavors for further reduction to III. In other words, both high CO₂ pressure and low temperature suppress further reduction and render the reduction terminating at the stage of the silyl formate, which leads to the formation of formamide V rather than VI.

Thirdly, reducing the amount of CO₂ to approx. 1 equiv. relative to amine delivers selectively VI rather than methylamine VII. When CO₂ (1 equiv. relative to amine) reacts with amine and diphenylsilane, CO₂ is quickly consumed, thus resulting in failure in conversion of VI to VII due to CO₂ deficiency and renders the reaction terminating at the step of aminal VI. That is, inadequate CO₂ amount restricts further reduction of VI to VII.

To sum up, CO_2 amount in this betaine catalysis determines product diversity (formamide, aminal and methylamine, respectively) as well as hierarchical reduction of CO_2 to formic acid (+II), formaldehyde (0) and methanol (-II) oxidation level.

In summary, we have developed an efficient organocatalytic process for reductive functionalization of CO_2 with amines and diphenylsilane promoted by glycine betaine. Through tuning the CO_2 amount and reaction temperature, this protocol enables three levels of reductive products with various energy content i.e. formamide, methylamine and aminal, which represents hierarchical reduction of CO_2 to formic acid, formaldehyde and methanol oxidation level, to be accessed respectively. This is the first time that switchable 2-, 4- and 6-electron reduction of CO_2 coupled with construction of C-N bond was realized under organocatalysis.

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Scheme 3. Proposed reaction pathway on reductive functionalization of CO₂ with amine to selectively afford formamide, methylamine and aminal

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Keywords: Carbon dioxide fixation, organocatalysis, betaine, hierarchical reduction, aminal

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- [24] Characterization data and NMR spectra of 1e were given in SI.
- [25] DFT study showed that the Si-H bond of hydrosilane is further polarized once coordinated with GB, resulting in the hydrosilane activation by GB, see SI.

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Hierarchical reduction of CO_2 : efficient and sustainable glycine betaine catalysis was developed for reductive functionalization of CO_2 with amines and diphenylsilane. Such organocatalysis afforded the products with diversified energy content i.e. formamide, aminal and methylamine respectively through hierarchical 2-, 4and 6-electron reduction of CO_2 coupled with C-N bond formation for the first time.



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