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COMMUNICATION

Synthesis of silyl formates, formamides, and aldehydes via solvent-free organocatalytic hydrosilylation of CO_2 †

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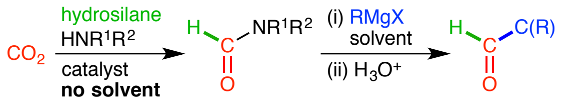
Carbon dioxide (CO_2) was used as a C1 source to prepare silyl formates, formamides, and aldehydes. Tetrabutylammonium acetate (TBAA) catalyzed the solvent-free *N*-formylation of amines with CO_2 and hydrosilane to give formamides including Weinreb formamide, Me(MeO)NCHO, which was successively converted into aldehydes by one-pot reactions with Grignard reagents.

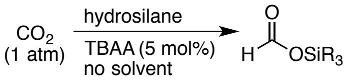
Carbon dioxide (CO_2) is an inexpensive and renewable chemical feedstock that has attracted much attention of chemists. Despite the kinetic and thermodynamic stability of CO_2, efficient and useful reactions have been developed.[1] Among various methods for CO_2 fixations, CO_2 reduction is becoming a hot research area,[2] and catalytic CO_2 reduction with hydrosilanes gives value-added substances.[3–5] Hydrosilylation of CO_2 can proceed stepwise to generate silyl formates (HCO_2SiR_3), bis(silyl)acetals ($CH_2(OSiR_3)_2$), methoxysilanes (CH_3OSiR_3), and methane, depending on reaction conditions.[3] A variety of metal catalysts and organocatalysts have been developed.[3–5] Furthermore, CO_2 and hydrosilanes can be combined with amines to effect *N*-functionalization such as *N*-formylation and *N*-methylation.[6,7] Even selective *N*-formylation/*N*-methylation of amines has been achieved simply by changing reaction parameters such as temperature and CO_2 pressure.[7] Polar aprotic solvents such as CH_3CN, DMF, and DMSO are often used.

Solvent-free reactions have great potential in sustainable organic synthesis.[8] As part of our ongoing efforts in solvent-free catalysis,[7i,9,10] we decided to search for a catalyst suitable for the solvent-free hydrosilylation of CO_2. The outline of our strategy is shown in Scheme 1, which involves the C–H bond formation without solvent and the subsequent one-pot C–C bond formation in solvent, for example, using an organometallic reagent such as a Grignard reagent (RMgX). Here we found tetrabutylammonium acetate (TBAA) as a catalyst for both the hydrosilylation of CO_2 and the *N*-formylation of amines in the presence of hydrosilane under solvent-free conditions, the latter of which gave various formamides including Weinreb formamide, Me(MeO)NCHO. Weinreb formamide was successively converted into aldehydes by one-pot reactions with Grignard reagents. This is a convenient and reliable method for one-pot aldehyde synthesis with CO_2.[11]



Scheme 1 Solvent-free *N*-formylation of amines and one-pot aldehyde synthesis.

Table 1 Solvent-free hydrosilylation of CO_2[a]



Entry	Hydrosilane	Temp. (°C)	Conv. (%)[b]	Yield (%)[c]
1	$PhMe_2SiH$	60	98	76
2	Ph_2MeSiH	60	97	70
3	Ph_3SiH	60	100	78
4	$PhSiH_3$	60	100	10
5	$PhSiH_3$	30	99	48

[a] Reaction conditions: CO_2 (1 atm), hydrosilane (2.0 mmol), TBAA (5 mol%), 8 h. [b] Conversion of silane. [c] Total yield of silyl formate and formic acid. Determined by ^1H NMR using mesitylene as an internal standard.

We screened several potential catalysts (5 mol%) for the solvent-free hydrosilylation of CO_2 (1 atm, balloon) with $PhMe_2SiH$ at 60 °C (Table S1 in ESI). As a result, tetrabutylammonium fluoride (TBAF) and TBAA successfully produced silyl formate (HCO_2SiMe_2Ph) in 52% and 76% yields, respectively. Control experiments without CO_2 or catalyst

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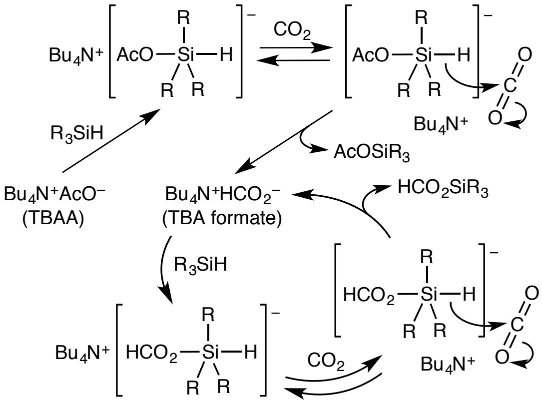
demonstrated that both of them were essential for the reaction. In contrast, other TBA halides and inorganic salts such as Cs_2CO_3 and CsF, some of which have been reported to work as catalysts in polar aprotic solvents,[5a] showed no catalytic activity under the present reaction conditions. These results are partly due to either insolubility in liquid hydrosilane or poor nucleophilicity. We employed TBAA for further investigations to confirm that TBAA was effective for several hydrosilanes (Table 1). $PhMe_2SiH$ and Ph_2MeSiH exhibited good reactivity at 60 °C (entries 1 and 2). Ph_3SiH, a solid at room temperature, melted at 60 °C, and the reaction proceeded to give the corresponding silyl formate (entry 3). In sharp contrast, the use of $PhSiH_3$ at 60 °C afforded the product in only 10% despite 100% conversion of $PhSiH_3$ (entry 4). Lowering temperature to 30 °C improved the yield to 48% (entry 5). The yields were modest probably because of a side reaction generating H_2 (ESI).



Scheme 2 A plausible reaction mechanism.

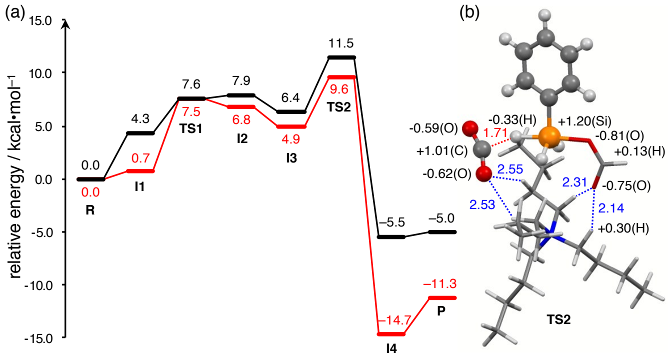
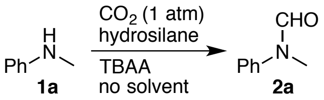


Fig. 1 (a) Energy profile for the hydrosilylation of CO_2 with $PhSiH_3$ and TBA formate. Potential energies and free energies (303 K) are shown in red and black, respectively. (b) Structure of **TS2** with distances (Å) in blue or red and NBO charges in black.

A plausible reaction mechanism is shown in Scheme 2. The nucleophilic attack of ^{-}OAc of TBAA on the Si atom of a hydrosilane gives a pentacoordinate silicate species. Subsequent hydride transfer to CO_2 gives silyl acetate ($AcOSiR_3$) and TBA formate ($Bu_4N^+HCO_2^-$), the latter of which is a catalytically active species (ESI).[5d] This HCO_2^- acts as a nucleophile to generate another pentacoordinate silicate species. Subsequent hydride transfer to CO_2 gives silyl formate (HCO_2SiR_3), regenerating TBA formate. TBA formate may react with $AcOSiR_3$ to give TBAA and HCO_2SiR_3, and in the case of $PhSiH_3$, the remaining H atoms on the Si atom can also be used for the reduction of CO_2 (not shown).[6e] This catalytic cycle was supported by DFT calculations, where $PhSiH_3$ was employed as a model hydrosilane (Fig. 1 and Fig. S5 in ESI).[12] All the components ($Bu_4N^+HCO_2^-$, $PhSiH_3$, and CO_2) are included in reactant complex **R**. The formate anion interacts weakly with the Si atom of $PhSiH_3$ to form a metastable complex **I1**, and a pentacoordinate silicate species **I2** generates via transition state **TS1** with a low energy barrier ($\Delta G^{\ddagger}$ = 7.6 kcal/mol). The pentacoordinate silicate species then makes a contact with CO_2 to give a weak complex **I3**. The subsequent hydride-transfer reaction reaches transition state **TS2** to afford intermediate **I4**, where the negatively charged O atom of HCO_2^- interacts with the Si atom of the silyl formate. The dissociation of the adduct gives silyl formate **P** with the regeneration of the catalyst. The desorption energy from **I4** to **P** is calculated to be ΔE = 3.4 kcal/mol ($\Delta G°$ = 0.5 kcal/mol). The whole energy profile clearly indicates that this reaction is exothermic and that the entropy term becomes negatively large in the later stage of the reaction as the number and symmetry of the molecules decrease. The highest-energy transition state **TS2** is only 11.5 kcal/mol higher than **R**, which indicates that this catalytic cycle is likely to occur at ambient temperature. The anionic species in the key transition state, **TS2**, is stabilized by the electrostatic field of the TBA cation and the hydrogen bonds of the formyl O atom of the pentacoordinate silicate species with the positively charged H atoms of the TBA cation (2.14 Å and 2.31 Å).[13]

Table 2 Solvent-free *N*-formylation of **1a**[a]



Entry	Hydrosilane	Temp. (°C)	TBAA (mol%)	Yield (%)[b]
1	$PhMe_2SiH$	60	5	42
2	Ph_2MeSiH	60	5	64
3	Ph_3SiH	60	5	72
4	Ph_2SiH_2	30	5	56
5	$PhSiH_3$	30	5	82
6	$PhSiH_3$	30	3	90
7	$PhSiH_3$	30	2	83
8	$PhSiH_3$	30	1	74
9[c]	PMHS	30	2.5	82

[a] Reaction conditions: **1a** (0.50 mmol), CO_2 (1 atm), hydrosilane (2.0 mmol), TBAA (loading % based on silane), 12 h. [b] Determined by ^1H NMR using mesitylene as an internal standard. [c] PMHS (400 µL, Si–H: 6 mmol).

We next examined the catalytic activity of TBAA for the solvent-free *N*-formylation of amines with CO_2 and hydrosilane. A mixture of *N*-methylaniline, hydrosilane, and TBAA was stirred under CO_2 (1 atm) for 12 h (Table 2). The use of $PhSiH_3$ at 30 °C gave the best result (entries 1–5). When the amount of TBAA was reduced to 1 mol%, the yield decreased to some degree (entries 6–8). When polymethylhydrosiloxane (PMHS), an inexpensive polymer containing the Si–H bond, was used as a reductant, the reaction took place efficiently at 30 °C (entry 9).

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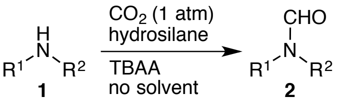
Substrate scope was investigated with $PhSiH_3$ or PMHS (Table 3). *N*-Methylanilines **1a**–**e** with the electron-withdrawing or electron-donating groups were successfully converted into *N*-methylformanilides **2a**–**e** in good yields. Other *N*-substituted anilines **1f**–**h** were also tolerated. More bulky amine **1i** was a poor substrate, while *N*-benzylmethylamine (**1j**) exhibited good reactivity.

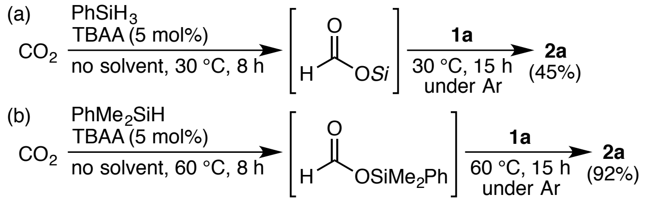
Table 3 Scope of solvent-free *N*-formylation of amines[a]



Entry	1	R^1	R^2	Yield (%)[b]	
				$PhSiH_3$	PMHS
1	**1a**	Ph	Me	76	63
2	**1b**	4-Cl-C_6H_4	Me	64	76
3	**1c**	4-Br-C_6H_4	Me	64	64
4	**1d**	4-OMe-C_6H_4	Me	64	76
5	**1e**	4-Me-C_6H_4	Me	91	89
6	**1f**	Ph	Et	97	77
7	**1g**	Ph	*n*-Pr	74	77
8	**1h**	Ph	$CH_2CH=CH_2$	58	82
9	**1i**	4-Me-C_6H_4	4-Me-C_6H_4	3	0
10	**1j**	$PhCH_2$	Me	69	72
11	**1k**	Me	OMe	95[c]	0

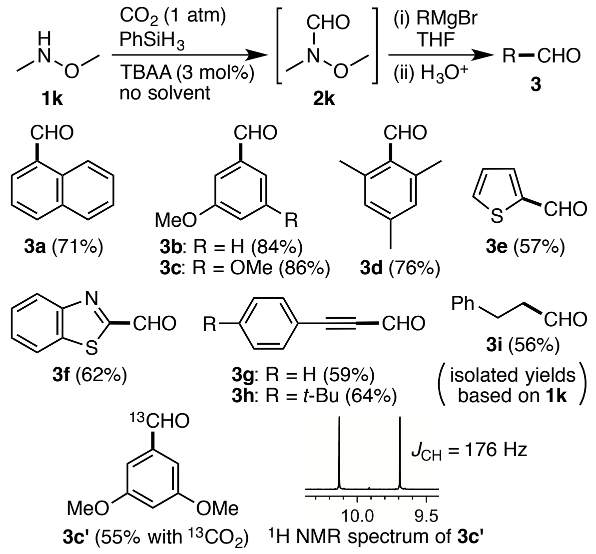
[a] Reaction conditions: **1** (0.50 mmol), CO_2 (1 atm), $PhSiH_3$ (2.0 mmol) or PMHS (400 µL, Si–H: 6 mmol), TBAA (5 mol% based on $PhSiH_3$ or 2.5 mol% based on PMHS), 30 °C, 12 h. [b] Isolated yield. [c] Reaction conditions: **1k** (2.0 mmol), CO_2 (1 atm), $PhSiH_3$ (2.0 mmol), TBAA (3 mol%), 0 °C, 1 h then 20 °C, 5 h. Yield determined by ^1H NMR using mesitylene as an internal standard.

Because various mechanisms have been proposed for *N*-formylation with different catalysts,[6a,6e,6g,7c,14,15] we conducted control experiments (Scheme 3). After the TBAA-catalyzed hydrosilylation of CO_2 with $PhSiH_3$ or $PhMe_2SiH$, CO_2 was replaced with Ar, and **1a** was then added to allow the reaction. As a result, **2a** was obtained in 45% or 92% yields, which suggests that **2a** was produced via the reactions of **1a** with silyl formates. This difference in productivity between $PhSiH_3$ and $PhMe_2SiH$ can be ascribed to the difference in water sensitivity between the corresponding silyl formates or intermediates.



Scheme 3 Control experiments.

The conversion of CO_2 into the formyl group of aldehydes is extremely important because of their considerable synthetic utility and value.[11] We envisioned that one-pot aldehyde synthesis might be achieved by taking advantage of the solvent-free C–H bond formation because any reagent and solvent could be added to the reaction mixture to effect the C–C bond formation (Scheme 1).[16] To realize this concept, we paid attention to Weinreb amides, which enable one to synthesize carbonyl compounds even with an excess amount of organometallic reagent.[17,18] We found that *N*,*O*-dimethylhydroxylamine (**1k**) could be successfully converted into *N*-methoxy-*N*-methylformamide (**2k**) under slightly modified conditions with $PhSiH_3$ (Table 3, entry 11). This is the first synthesis of Weinreb formamide **2k** from CO_2. Subsequently, the reaction mixture was cooled in an ice bath, and a suspension of a Grignard reagent (RMgBr) in THF, which was prepared from either RBr or RH, was added under N_2. After stirring at 0 °C for 2 h, the reaction was quenched. To our delight, the C–C(sp^3, sp^2, or sp) bond was formed to give various aldehydes **3** such as (hetero)aromatic aldehydes **3a**–**f**, propynals **3g**–**h**, and aliphatic aldehyde **3i** in good to high yields (Scheme 4). ^1H and ^{13}C NMR spectra of **3c'** synthesized with $^{13}CO_2$ showed a doublet at 9.91 ppm (J_{CH} = 176 Hz) and an intense singlet at 192.1 ppm (ESI), respectively, which clearly demonstrates that the carbon atom of the formyl group originated from carbon dioxide. In contrast, one-pot reactions of Grignard reagents with HCO_2SiMe_2Ph instead of Me(MeO)NCHO resulted in no formation of aldehydes.



Scheme 4 One-pot synthesis of aldehydes.

In summary, tetrabutylammonium acetate (TBAA) worked as a catalyst for the solvent-free hydrosilylation of CO_2 (1 atm). DFT calculations indicated that TBA formate generated in situ is a catalytically active species. TBAA was also effective for the *N*-formylation of amines with CO_2 (1 atm) and hydrosilanes to give various formamides, including Weinreb formamide, Me(MeO)NCHO. Taking advantage of solvent-free conditions, Weinreb formamide was successively converted into aldehydes by one-pot treatment with Grignard reagents. This achievement is significant because various reactions with different substrate/reagent/catalyst/solvent can be employed in the second step of one-pot synthesis (Scheme 1). This strategy is a new entry to one-pot C–H/C–C bond formation with CO_2.[11,16,19]

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Conflicts of interest

There are no conflicts to declare.

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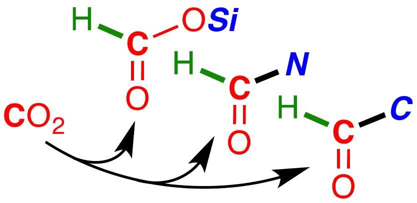

Silyl formates, formamides, and aldehydes were synthesized via the solvent-free hydrosilylation of carbon dioxide using tetrabutylammonium acetate as a catalyst.