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Mechanistic Study of the N-Formylation of Amines with Carbon Dioxide and Hydrosilanes

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ABSTRACT: N-formylation of amines with CO₂ and hydrosilane reducing agents proceeds via fast and complex chemical equilibria, which hinder easy analysis of the reaction pathways. *In-situ* reaction monitoring and kinetic studies reveal that the three proposed pathways, direct- or amine-assisted formoxysilane formation (pathways 1 and 2, respectively) or via a silylcarbamate intermediate (pathway 3), are possible depending on the reaction conditions and the substrates. While pathway 1 is favored for non-nucleophilic amines in the absence of a catalyst, a base catalyst results in non-innocent behavior of the amine in the CO₂ reduction step towards the formoxysilane intermediate. The reaction pathway is altered by strongly nucleophilic amines, which form stable adducts with CO₂. Silylcarbamate intermediates form, which can be directly reduced to the N-formylated products by excess hydrosilane. Nevertheless, without excess hydrosilane, the silylcarbamate is an additional intermediate en-route to formoxysilanes along pathway 2. Exchange NMR spectroscopy (EXSY) revealed extensive substituent exchange around the hydrosilane silicon center, which confirms its activation during the reaction and supports the proposed reaction mechanisms. Numerous side reactions were also identified, which help to establish the reaction equilibria in the N-formylation reactions.

Key words: Carbon dioxide, Reduction, N-formylation, Hydrosilane, Ionic liquid, Catalysis

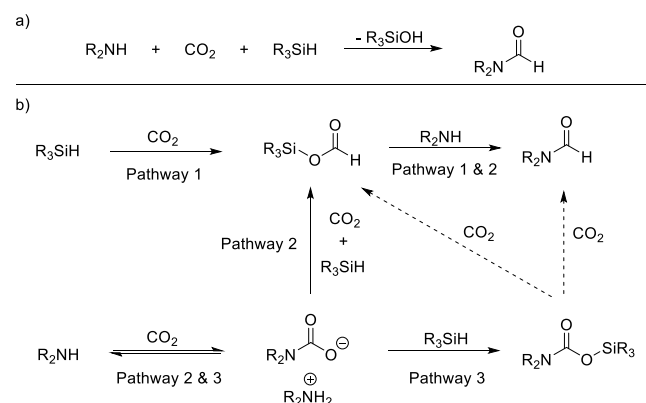
Introduction

Amine reactions with CO₂ and hydrosilanes have attracted considerable attention in recent years.^{1–3} Formamide, N-methylamine and amination products are highly valuable building blocks in chemical synthesis.^{2,4} Moreover, CO₂ is a cheap, non-toxic and abundant C1 source⁵ and hydrosilanes are convenient, mild and easy to use reducing agents (polymethylhydrosiloxane, PMHS, for example, is a waste product of the silicon industry and is inexpensive).⁶ Consequently, a large number of catalysts have been developed for this reaction including simple metal salts, complexes based on Rh,⁷ Ru,⁸ Re,⁹ W,¹⁰ Cu,^{11,12} Zn,^{13,14} and Fe,¹⁵ and transition metal-free catalysts such as carbenes,^{6,16–18} guanidines,¹⁹ zwitterionic P-ylide-CO₂ adducts,²⁰ 1,3,2-diazophospholones,²¹ carboxylates,^{22,23} carbonates,²⁴ ionic liquids,^{25,26} triazabicyclodecene (TBD),^{27,28} and γ -valerolactone.²⁹ In addition, the solvents typically used, i.e. DMSO and DMF, are catalytically active.³⁰ Interestingly, the organocatalysts can catalyze multiple CO₂-hydrosilane reactions leading to more than one of the abovementioned products or even all of them depending on the conditions employed.^{6,18,27,28,31}

The observed selectivity, or lack of, generated interest in the reaction pathways that lead to the individual formamide, N-methylamine and amination products.³ With N-formylated products, most recent evidence suggests that three possible pathways can take place involving two different intermediates (Scheme 1).¹⁹ Pathway 1 involves direct reduction of CO₂ by the hydrosilane, to form a formoxysilane intermediate, followed by a simple addition-elimination reaction with the amine to

form the formamide product. Hydrosilane activation by a nucleophilic catalyst and CO₂ reduction by a hypervalent silicon was proposed as the transition state (TS).^{22,24,26,31} The pathway is supported by DFT calculations³² and the isolation and reactivity of the formoxysilane intermediate.³³ However, more recent DFT calculations suggest that this pathway is favored in the absence of a catalyst,³⁴ but otherwise is likely to be slow.¹⁹ Pathway 2 also involves a formoxysilane intermediate and its subsequent reaction with an amine to form the formamide product. However, its formation is dependent on a catalyst stabilized carbamate salt, which activates the hydrosilane in a similar manner to that proposed for pathway 1 with a comparable TS.³⁵ DFT calculations of the reaction mechanism with NHC-carbene and ZnCl₂ catalysts indicate that the energy of pathway 2 is lower than that for pathway 1.^{35,36} Nevertheless, based on the N-formylation of morpholine with phenylsilane and 1,1,3,3-tetramethylguanidine catalyst, stable carbamate salts react with phenylsilane to form a silylcarbamate, rather than the formoxysilane previously reported, pathway 3.¹⁹ The silylcarbamate intermediate is then transformed to the formamide product in the presence of CO₂, either via the formoxysilane or directly by a different mechanism. An alternative pathway, via water sensitive silylamines, towards the silylcarbamate was also proposed,³⁰ but has since been ruled out as unfeasible under the reaction conditions normally employed and due to its extreme moisture sensitivity.¹⁹

Scheme 1: N-formylation of amines with CO₂ and hydrosilanes



a) General reaction scheme. b) Previously proposed reaction pathways.

Irrespective of the reaction pathway, it became apparent that the reaction proceeds by a series of fast and complex chemical equilibria.¹⁹ This complexity, combined with the instability of the intermediates, hinders identification of the reaction pathway. Difficulties with the gas-liquid binary system largely restricted mechanistic investigations to *ex-situ* analysis of the reaction intermediates by ¹H, ¹³C and ²⁹Si NMR spectroscopy and FTIR spectroscopy or stepwise addition experiments.^{19,25,30,31} Hence, we decided to investigate and establish the chemical equilibria as well as the reaction kinetics involved in the N-formylation reaction *in-situ* using NMR spectroscopic techniques. The effects of the amine and hydrosilane on the equilibria as well as the reaction pathway were investigated and, finally, a number of conditions governing the reaction pathway and observed intermediates were identified.

Reactions were primarily carried out in DMSO-d₆ with N-methylaniline and phenylsilane at 25°C and 20 bar CO₂ pressure. However, other anilines as well as benzylamine and triethoxysilane were used to provide further insights. Low temperatures and high pressures were used to suppress the formation of N-methylamines and amination side products, which require higher temperatures and, based on the pathways proposed, sequential reduction of CO₂ by the hydrosilane.^{19,22,31} Tetrabutylammonium acetate ([TBA][OAc]) was selected as a representative oxygen-containing nucleophilic,^{20,22–24} ionic liquid-like,^{25,26} basic^{19,27,28} catalyst.

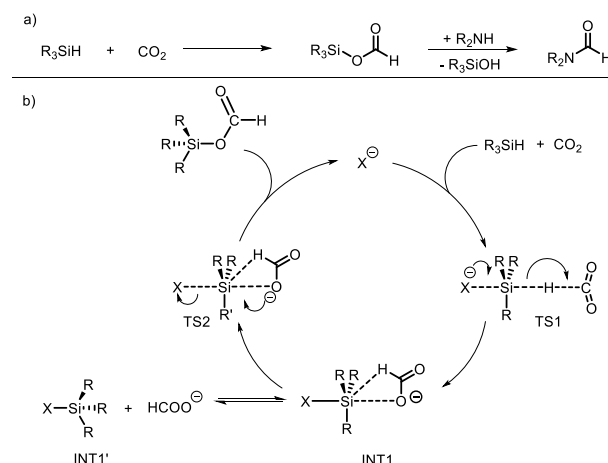
Results and discussion

Pathway 1 and CO₂-hydrosilane chemical equilibria

In the absence of a catalyst, reduction of CO₂ and the formation of the formoxysilane intermediate was identified by DFT calculations as the rate-determining step in the N-formylation reaction of N-methylaniline with phenylsilane.³⁴ Simultaneously, hydrosilane activation by nucleophilic catalysts was proposed as the mode-operandi for a number of N-formylation catalysts including NHC-carbenes,³² tetrabutylammonium fluoride ([TBA][F]),²⁶ Cs₂CO₃,²⁴ glycine beta-

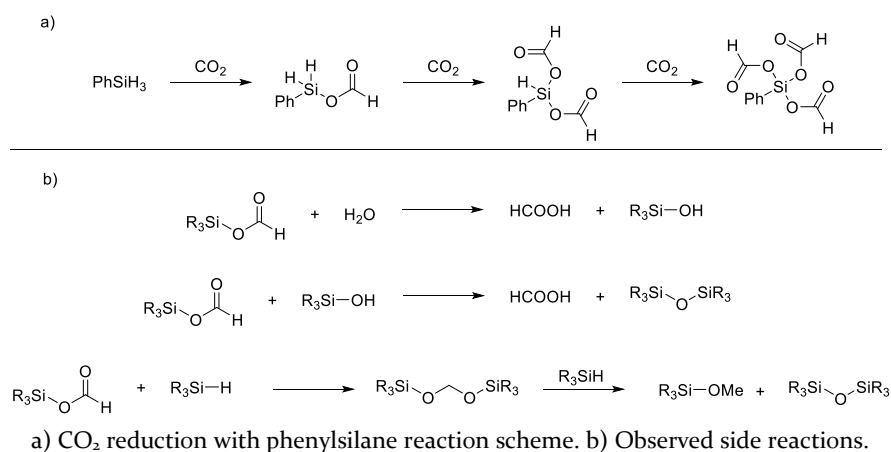
ine³¹ and various carboxylates²² (Scheme 2). Clearly, the mechanism of CO₂ reduction and the formation of the formoxysilane intermediate is key to understanding pathway 1. In addition, all N-formylation catalysts should catalyze the reduction of CO₂ to formoxysilane (or formic acid after hydrolysis) in the absence of an amine. Notably, direct reduction of CO₂ to formoxysilane was demonstrated with NHC-carbenes³⁷ and [TBA][F]³⁸ catalysts, which provided part of the basis for pathway 1.

Scheme 2: Pathway 1 for the N-formylation of amines



a) Pathway 1 reaction scheme b) Proposed mechanistic cycle for the rate determining CO₂ reduction step.^{23,35} X[−] represents a general nucleophilic anion such as OAc[−], F[−] or CO₃^{2−} proposed to follow pathway 1.

Experiments with [TBA][OAc] (10 mol%) showed that the salt catalyzes CO₂ reduction with phenylsilane, decreasing the reaction time from over 13 h to < 6 h (Figures S2 and S9), to afford a mixture of formoxysilanes, formic acid and, in extremely low yield, bis(silylacetals) and methoxysilane side-products.³⁷ Post-reaction analysis of the reduction of CO₂ with triethoxysilane by GC-MS also indicated the presence of tetraethoxysilane (vide infra) and various siloxanes, which could not be identified with certainty by NMR spectroscopy due to extensive overlap of the peaks. Formic acid probably results from formoxysilane hydrolysis due to trace water in the reaction solvent as its concentration does not change after the first 30 minutes of reaction. Bis(silylacetals), methoxysilanes and siloxanes are products from the reduction of formoxysilane with the hydrosilane.³⁷ Silanols potentially produced by formoxysilane hydrolysis were not detected (Figure 1) indicating that they react further with formoxysilanes to generate formic acid and siloxanes (Scheme 3). It should be noted that siloxanes can also be formed from the reaction of silanols with (unreacted) hydrosilane generating hydrogen as the by-product.³⁹ Considering that water is usually not rigorously excluded from N-formylation reactions it is highly probable that formic acid is formed and reduces the overall yield or at least the amount of hydrosilane available for reaction.

Scheme 3: CO₂ reduction with phenylsilane at 20 bar pressure

Larger quantities of bis(silylacetals), methoxysilanes and siloxanes could also be expected due to lower pressures usually employed, decreasing the rate of formation of formoxysilane and increasing the rate of its reduction.¹⁹

The presence of formic acid in the reaction hinders accurate analysis of the formoxysilane(s) formed as these are usually identified by a distinct formyl (-CHO) proton signal in their ¹H NMR spectra. In the reaction of phenylsilane at 25°C this signal overlaps with the signal from formic acid resulting in a broad peak (Figure 1), which, however, moves from 8.24 to 8.16 ppm as the reaction progresses. Hence, at 25°C in DMSO-d₆ the presence of formoxysilane is only indicated by the uneven integration of the acidic signal at 12.76 ppm and the broad -CHO signal between 8.24 and 8.16 ppm.

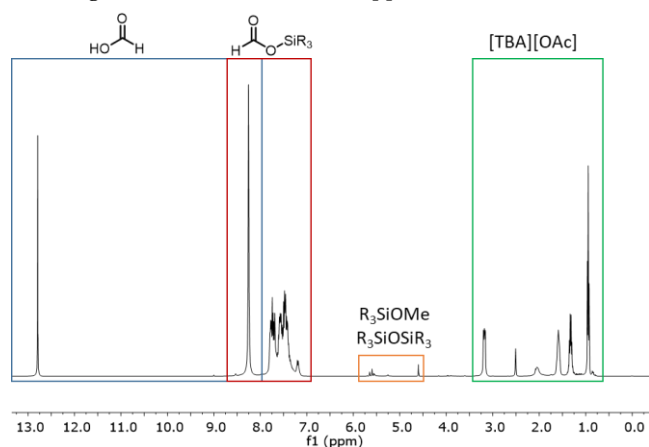
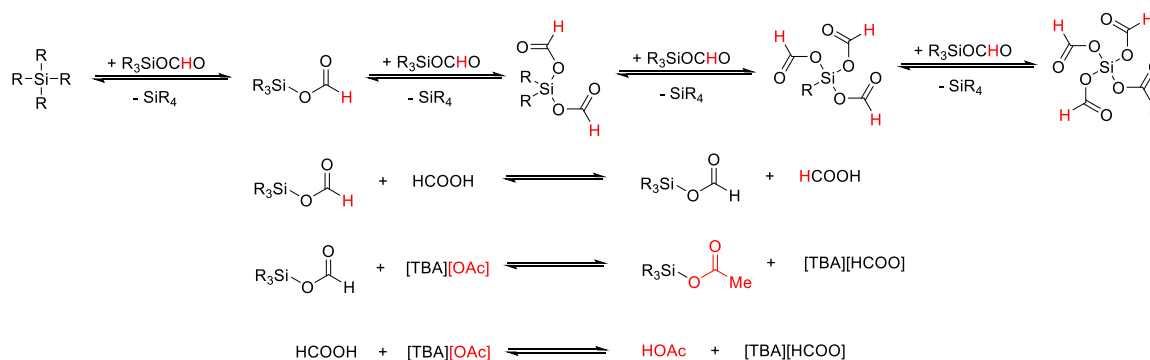


Figure 1: ¹H NMR spectrum of the reduction of CO₂ with phenylsilane after 13 h (i.e. at the end of the reaction).

Since broad signals are indicative of substituent exchange, the reaction was gradually cooled to 218 K in DMF-d₇ confirming the presence of a dynamic exchange process between formic acid and formoxysilane(s). Surprisingly, the broad singlet attributed to -CHO splits into four different signals at 8.51, 8.69, 8.70 and 8.74 ppm rather than the expected two for formic acid and the formoxysilane PhSi(OCHO)₃ (Figures S3 and S4). Similar changes were observed in the ¹³C NMR spectra, but

only broadening of the peaks in the ²⁹Si NMR spectra is observed, indicating close proximity of multiple signals and/or continuous rapid exchange of the Si substituents. Incomplete conversion of phenylsilane to PhSiH(OCHO)₂ and PhSiH₂(OCHO) was ruled out by the absence of any Si-H signals in both the ¹H and ²⁹Si NMR spectra (Figure S7), indicating the formation of other formyl species in solution. Large changes in the ¹H NMR spectra were also observed in the aromatic region and for the signals corresponding to the [TBA][OAc] catalyst (vide infra). Exchange spectroscopy (EXSY) revealed interchange of the formyl groups between formic acid and the three other -CHO containing compounds as well as the exchange of phenyl groups between various species in solution (Figure S5). Even at 218 K the -CHO signals were broad and not fully resolved, confirming exchange on the NMR time scale and limiting the analysis. The full extent of the exchange was revealed with triethoxysilane (Scheme 4). Triethoxysilane can reduce one CO₂ molecule to formoxysilane EtO₃SiOCHO. However, in DMSO-d₆ at room temperature, five peaks attributable to the -CHO moiety at 8.13, 8.25, 8.31, 8.34 and 8.35 ppm gradually form, of which the one at 8.35 ppm was consumed during the course of the reaction and the one at 8.13 ppm corresponds to the C-H proton in formic acid. In DMF-d₇ upon cooling to 218 K the remaining peaks were attributed to three different formoxysilanes (with peaks at 8.44, 8.54 and 8.59 ppm) as well as to formic acid (at 8.32 ppm). EXSY at 258 K showed exchange of the formyl group between formic acid and the formoxysilanes and also exchange among the various formoxysilanes (Figure 2). Due to extensive overlap of the peaks from the ethoxy substituents, exchange of these groups could not be unambiguously confirmed, but is implied by the large number of ethoxy signals and the detection of tetraethoxysilane (which gives peaks at 3.78 and 1.17 ppm in the ¹H NMR spectrum and at -82 ppm in the ²⁹Si NMR spectrum). The presence of tetraethoxysilane was further confirmed by GC-MS at the end of the reaction. Finally, the formyl signals were assigned to formic acid, R₃SiOCHO, R₂Si(OCHO)₂, RSi(OCHO)₃ and Si(OCHO)₄, where R = Ph or EtO. The formation of these four formoxysilanes is accompanied by the simultaneous formation of SiR₄ supported by the observed exchange of phenyl groups and confirmed by the formation of tetraethoxysilane.

Scheme 4: Exchange reactions that take place during the reduction of CO₂ with hydrosilanes


Substituent exchange has been observed in the related hydrosilane reduction of carbonyls catalyzed by fluoride salts and bases.⁴⁰ The reaction proceeds by hydrosilane activation with a nucleophilic catalyst and a five-membered hypervalent silicon intermediate. Similarly, a five-membered silicon intermediate was proposed for the hydrosilane reduction of CO₂.²⁶ DFT calculations demonstrated that a related five-membered TS, rather than an intermediate, is energetically favored in CO₂ reductions.³⁵ However, similar exchange behavior is still expected and confirmed by the EXSY experiments further supporting the proposed reaction mechanism. Hence, a binuclear associative mechanism,⁴⁰ possibly assisted by a bridging carboxylate anion may be involved in the exchange process. In addition, the exchange can potentially be exploited for the preparation of highly reactive formoxysilanes from hydrosilanes of inherently low reactivity, similarly to the recently reported preparation of gaseous hydrosilanes from alkoxyhydrosilane surrogates in the reduction of alkenes.⁴¹

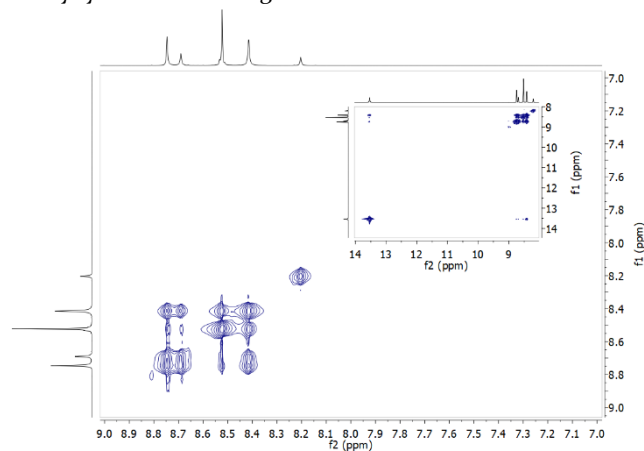


Figure 2: EXSY NMR spectrum of the products from the reaction of EtO₃SiH and CO₂ at 258 K. For full Spectrum Figure S17.

DFT calculations suggest that an off-cycle species may be derived en-route to formoxysilane in which the acetate anion attaches to the hydrosilane to eliminate a formate anion (INT1', Scheme 2).²³ This behavior was observed with iridium trifluoroacetate complexes, where detachment of the ligand and its reaction with hydrosilane and CO₂ resulted in partial catalyst deactivation.³⁹ However, considering the substituent exchange process around the silicon center, a dynamic exchange

of the acetate anion with the formate anion is expected with the [TBA][OAc] catalyst. Indeed, with phenylsilane the acetate peak broadened and shifted to higher frequency during the reaction. Upon cooling to 218 K three partially overlapping peaks are observed (Figure S4). In the reactions of triethoxysilane the acetate ¹H NMR signal splits into two distinct peaks at 1.91 and 2.09 ppm. The former corresponds to [TBA][OAc] and the latter may be assigned to the silane bound acetate, R₃SiOAc, the assignment of which is supported by comparison with separately prepared EtO₃SiOAc.⁴² Dynamic exchange between the two species was confirmed by EXSY NMR experiments (Figure S17). Incorporation of the anion in the substituent exchange process was confirmed by the use tetrabutylammonium formate ([TBA][HCO₂]) instead [TBA][OAc]. With [TBA][HCO₂], upon addition of CO₂, the peak corresponding to the formate anion disappears and only peaks attributable to formoxysilanes and the tetrabutylammonium cation are observed (Figures S21 and S22), confirming that the anion of the catalyst is involved in the exchange equilibrium. Proton exchange was also detected between the formyl –CHO protons and the formic acid –OH protons, which cannot be explained by a five-membered silicon mediated transfer. However, such exchanges are known for reversible reductions of CO₂ to formic acid with dihydrogen⁴³ indicating, at least in part, that formation of the formoxysilane is reversible, i.e. the hydrosilane and CO₂ can reform.

Finally, N-methylaniline was added to the reaction mixture and the consumption of phenylsilane (Figure 3) as well as the formation of N-methylformanilide was monitored. In the absence of the [TBA][OAc] catalyst, phenylsilane was consumed at the same rate irrespective of whether N-methylaniline is present or not. In addition, N-methylformanilide forms at a comparable rate to formoxysilane. The rate of phenylsilane consumption in the presence of the [TBA][OAc] catalyst is considerably faster in the presence of N-methylaniline (compared to the reaction without N-methylaniline). The phenylsilane was completely consumed within 1 hour in contrast to 6 hours in the absence of N-methylaniline. Considering that formoxysilane formation was identified as the rate-determining step of pathway 1,³⁴ the absence of any intermediates is as expected. The equivalent CO₂ reduction rates without the [TBA][OAc] catalyst concur with DFT calculations that pathway 1 is the preferred N-formylation route for N-methylaniline in the absence of a catalyst.

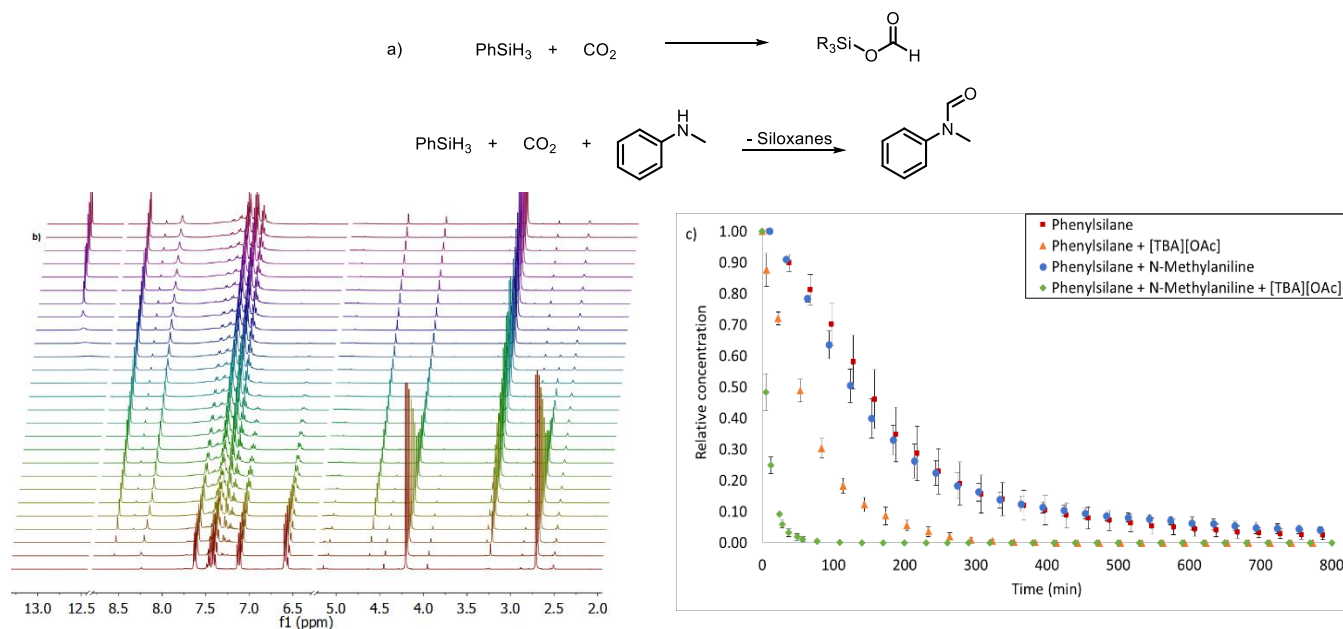


Figure 3: a) Reaction of phenylsilane with CO_2 in the presence and absence of N-methylaniline. b) Example of the ^1H NMR spectra of the N-formylation of N-methylaniline with PhSiH_3 under CO_2 (20 bar) over a period of 13 h. For full spectra Figure S28. c) Consumption of phenylsilane over the course of the reactions – see inset for details. General reaction conditions: phenylsilane (0.5 mmol), N-methylaniline (0.5 mmol), $\text{DMSO}-d_6$ (0.5 ml), [TBA][OAc] (10 mol%), CO_2 (20 bar), 298 K.

However, results with [TBA][OAc] demonstrate that N-methylaniline provides an alternative, much faster pathway for CO_2 reduction. Similar observations were made when triethoxysilane was employed as the reducing agent (Figures S11 and S31).

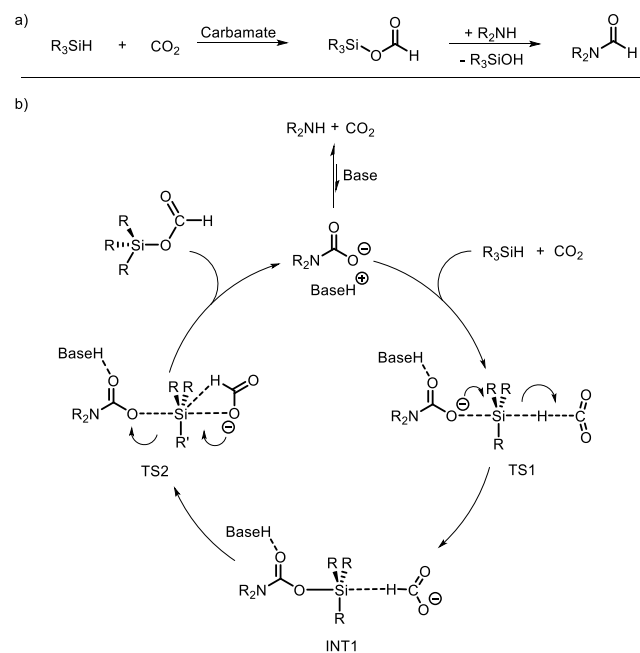
Overall, the reduction of CO_2 with hydrosilanes results in a mixture of formoxysilanes with continuous substituent exchange around the silicon center. An off-cycle species, $\text{R}_3\text{Si}-\text{OAc}$, forms during the reaction, resulting in the partial transformation of the catalyst to [TBA][HCO₂]. Formic acid and various siloxanes are the main reaction side products with the formation of bis(silylacetals) and methoxysilane in less than 2% yield. The formoxysilanes formed react with amines to form the formamide products.³³ However, pathway 1 is only accessible for N-methylaniline in the absence of a catalyst as proposed by DFT calculations.³⁴ Although [TBA][OAc] can activate hydrosilanes for direct CO_2 reduction, N-formylation of amines proceeds along a different, much faster pathway in the presence of this catalyst.

Pathway 2 and role of the amine

Pathway 2 was proposed based on computational studies and the observation of the formoxysilane intermediate.^{35,36} In contrast to pathway 1, the catalyst acts to stabilize the formation of a carbamate salt formed from the reaction of the amine with CO_2 , rather than activate the hydrosilane. The reaction of amines with CO_2 to form carbamate salts is well established and used on industrial scale to scrub CO_2 from various gas streams.⁴⁴ However, not all amines form stable carbamate salts, including N-methylaniline. Base catalysts help to stabilize the salt, which then activates the hydrosilane in a similar manner to that proposed in pathway 1 (Scheme 5). In addition, a base catalyst can accelerate the subsequent reaction be-

tween the amine and the formed formoxysilane.³⁵ Interestingly, all the nucleophilic catalysts including [TBA][OAc],²³ fluorides,²⁶ carbonates²⁴ and NHC-carbenes^{6,16–18,45} are also basic. Furthermore, non-nucleophilic bases such as TBD^{27,28} and guanidines¹⁹ catalyze the N-formylation reaction. A general base catalyzed reaction mechanism would thus encompass the majority of organic and salt catalysts.

Scheme 5: Pathway 2 for the N-formylation of amines



a) Pathway 2 reaction scheme. b) Proposed mechanistic cycle for the rate determining CO_2 reduction step.³⁵

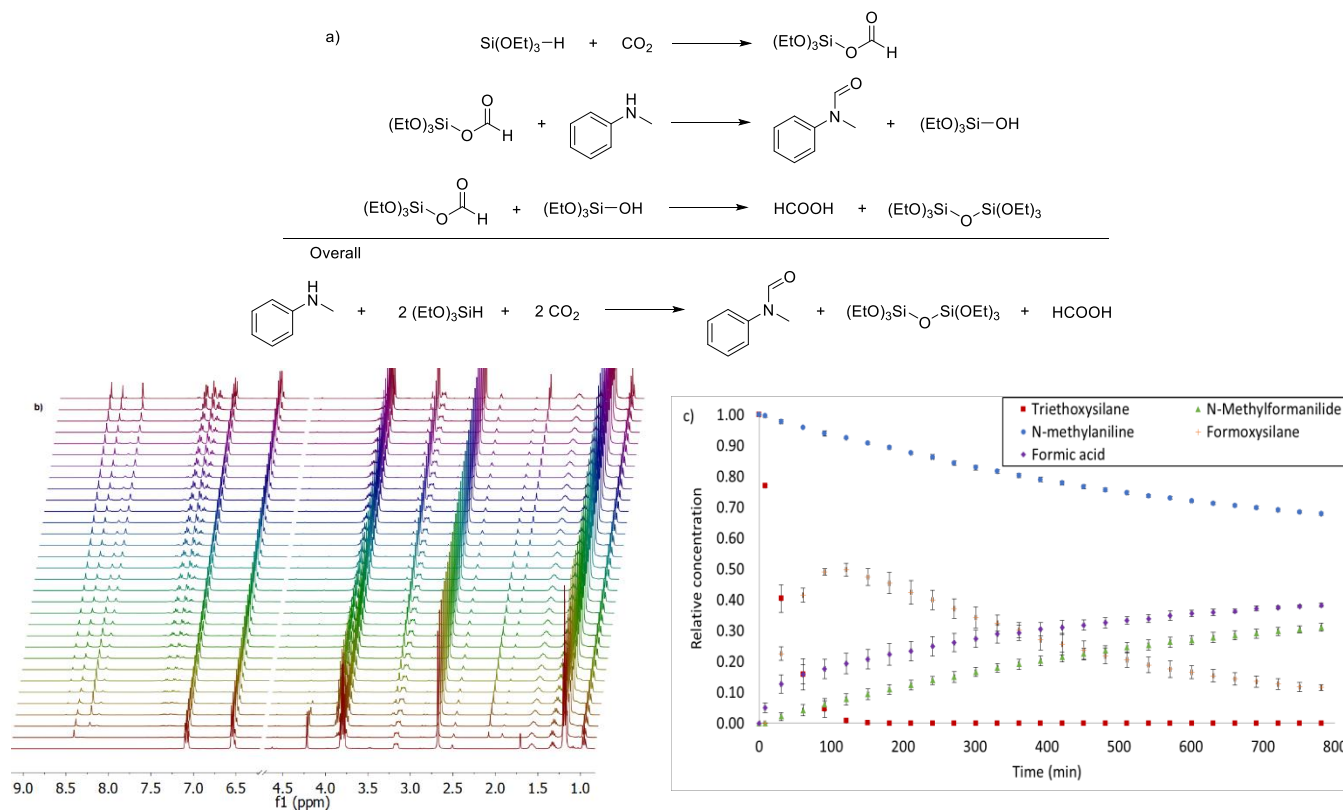


Figure 4: a) N-formylation of N-methylaniline with CO_2 and triethoxysilane and its side reactions and by-products. b) ^1H NMR spectra of N-methylaniline N-formylation with EtO_3SiH under CO_2 (20 bar) over a period of 13 h. For full spectra Figure S30. c) Kinetic curves for the formylation of N-methylaniline using triethoxysilane. Reaction conditions: triethoxysilane (0.5 mmol), N-methylaniline (0.5 mmol), DMSO-d_6 (0.5 ml), $[\text{TBA}][\text{OAc}]$ (10 mol%), CO_2 (20 bar), 298 K.

Kinetic studies of N-methylaniline formylation with phenylsilane and the $[\text{TBA}][\text{OAc}]$ catalyst reveal that the amine influences the rate of CO_2 reduction with hydrosilanes (Figure 3). In addition, the N-methylformanilide product forms at the same rate as the phenylsilane is consumed and no intermediates were detected. The only noticeable changes in the NMR spectra during the course of the reaction is a broadening of the $-\text{NH}$ signal of the N-methylaniline and loss of its coupling to the methyl group upon addition of CO_2 , indicating partial formation of a carbamate salt. However, a peak corresponding to the carbamate carbon was not detected by ^{13}C NMR spectroscopy, which supports the transient nature of such a salt even in the presence of a base catalyst. Both pathways 2 and 3 were proposed to proceed by the formation of a carbamate salt, with different intermediates derived from the carbamate salt proposed for each route.^{19,35,36} Identifying the intermediate, either a formoxysilane or a silylcarbamate, that leads to the product is key for distinguishing between pathways 2 and 3. However, the only compounds identified were phenylsilane, N-methylaniline, N-methylformanilide, formic acid and some minor side products, i.e. bis(silylacetal)s and methoxysilane. The presence of formic acid slightly favors pathway 2 over pathway 3 as the intermediate in formation of formic acid is formoxysilane.⁴⁶ However, the side products and by-products observed during the formation of a silylcarbamate have not been previously reported and, as such, the

presence of formic acid does not distinguish between the two pathways.

Ex situ reaction of the formoxysilane, $\text{EtO}_3\text{SiOCHO}$, with N-methylaniline to N-methylformamide has been reported.³³ Monitoring the reaction of N-formylation with triethoxysilane revealed the formation of at least three different formoxysilanes, identified by the appropriate $-\text{CHO}$ signals in the ^1H , ^{13}C and ^{29}Si NMR spectra (Figures S33-S35) and facilitated by comparison to spectra recorded for CO_2 reduction reactions in the absence of N-methylaniline. Two of the three formoxysilanes were gradually consumed during the reaction at 298 K, whereas the remaining formoxysilane reacted rapidly only after heating to 378 K. Simultaneous N-formanilide formation was observed further supporting pathway 2 (Figure 4). However, when all of the starting triethoxysilane was consumed it became apparent that two equivalents of formoxysilane are required to obtain N-methylformanilide as the formoxysilanes were consumed at twice the rate at which the N-methylformanilide was formed. As formic acid forms at an equivalent rate to the N-methylformanilide and no silanol by-product was observed, it seems likely that the silanol produced rapidly reacts with formoxysilane to generate various siloxanes and formic acid, as observed in the earlier reactions.

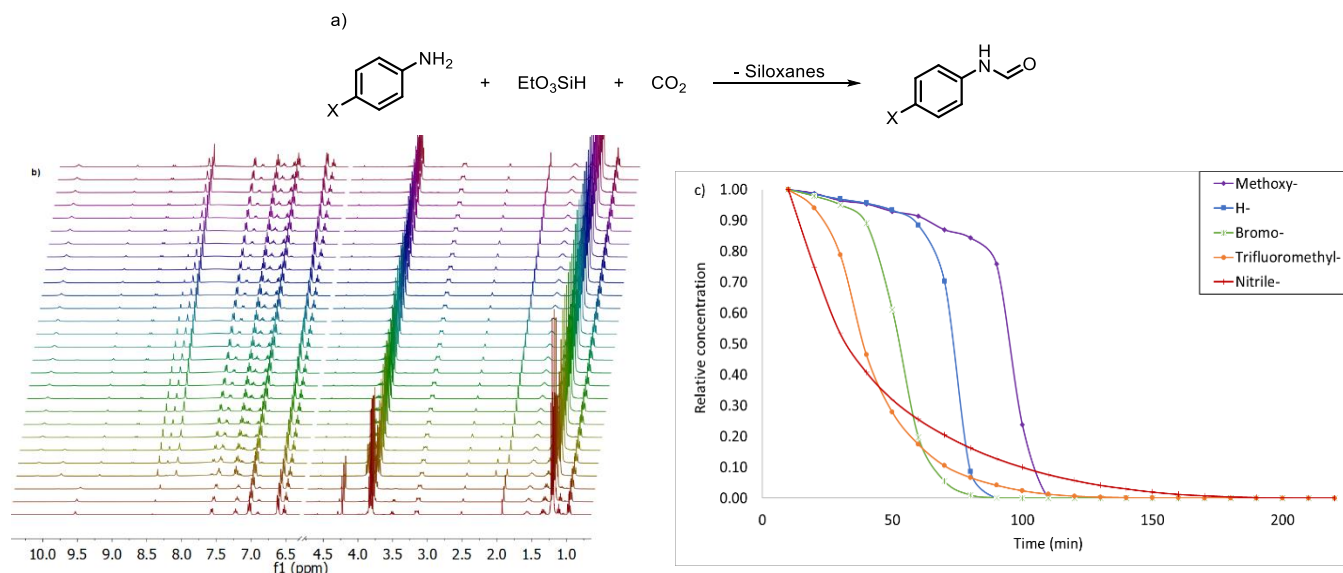


Figure 5: a) Reaction of p-substituted anilines with CO₂ and triethoxysilane. b) Example of the ¹H NMR spectra of the N-formylation of aniline with EtO₃SiH under CO₂ (20 bar) over a period of 13 h. For full spectra Figure S51. c) Consumption of triethoxysilane in the N-formylation reactions of methoxyaniline, aniline, bromoaniline, trifluoromethylaniline and 4-aminobenzonitrile. Reaction conditions: triethoxysilane (0.6 mmol), aniline (0.5 mmol), DMSO-d₆ (0.5 ml), [TBA][OAc] (10 mol%), CO₂ (20 bar), 298 K

The presence of EtO₃SiOSiOEt₃, as well as higher weight siloxanes was confirmed by GC-MS at the end of the reaction. Excess formic acid, in comparison to N-methylformanilide, may be attributed to the rapid initial reaction of formoxysilane with trace water present in the solvent. Overall, two equivalents of hydrosilane and CO₂ are required to produce one equivalent of N-methylformanilide with the simultaneous formation of formic acid and a siloxane (Figure 4a).

The formation of formoxysilanes and their reaction with N-methylaniline confirms that the N-methylformanilide is formed via pathway 2 in the presence of the [TBA][OAc] catalyst. In addition, pathway 2 proceeds via a similar five-membered hypervalent silicon TS to pathway 1 (Schemes 2 and 5),³⁵ which allows for exchange around the silicon center, substantiated by the multiple formoxysilanes observed rather than EtO₃SiOCHO alone. The substituent exchange process was confirmed by EXSY experiments (Figure S36). Interestingly, exchange between the acetate anion (observed at 1.93 ppm) and silane bound acetate (observed at 2.09 ppm) also takes place indicating that pathway 1 may compete with pathway 2 during N-methylaniline formylation or that the [TBA][OAc] catalyst is, at least in part, transformed to [TBA][HCO₂] or deactivated following reaction of the acetate with the silicon center.

To ascertain the role of the amine and the related carbamate salt on the reaction a series of p-substituted anilines were N-formylated under the standardized reaction conditions using triethoxysilane. The progress of the N-formylation reactions was monitored by ¹H NMR spectroscopy and the rate of hydrosilane consumption recorded (Figure 5). Both the reaction rate and the entire reaction kinetics demonstrated a strong dependence on the nature of the amine. As the basicity of the

amine and the stability of the carbamate salt increases an induction period for the N-formylation reaction is observed, followed by a sudden and rapid depletion of the triethoxysilane and amine, but without the formation of the product (Figures S52 and S56). Instead, an intermediate presumed to be silylcarbamate,¹⁹ from which the product forms, was observed (vide infra). Formoxysilanes were also detected, and as the basicity of the amine increases, they are consumed more rapidly. Only 4-aminobenzonitrile and to some extent 4-trifluoromethylaniline undergo direct observable conversion of formoxysilanes to their respective N-formylated products (Figures S40 and S44). In all other cases, formation of a new silylcarbamate intermediate dominates the reaction. Apparently, as the basicity of the amine increases, pathway 2 is gradually suppressed and pathway 3 becomes the dominate reaction pathway.

Thus, N-methylaniline formylation proceeds via pathway 2, as previously proposed by DFT calculations.³⁵⁻³⁶ A mixture of formoxysilanes with different reactivities is formed, which then react with N-methylaniline to form the desired product. However, two equivalents of Si-H and CO₂ are required for the N-formylation reaction due to simultaneous formation of a siloxane and formic acid. Nevertheless, the reaction pathway is not universal for all amines, but appears to operate only for amines of low basicity, which do not form stable carbamate salts. An alternative reaction pathway with an additional intermediate is responsible for the N-formylation of more basic amines. The transition from pathway 2 to pathway 3 does not appear immediately, but rather as a gradual transition, where both pathways compete with each other with amines of intermediate basicity.

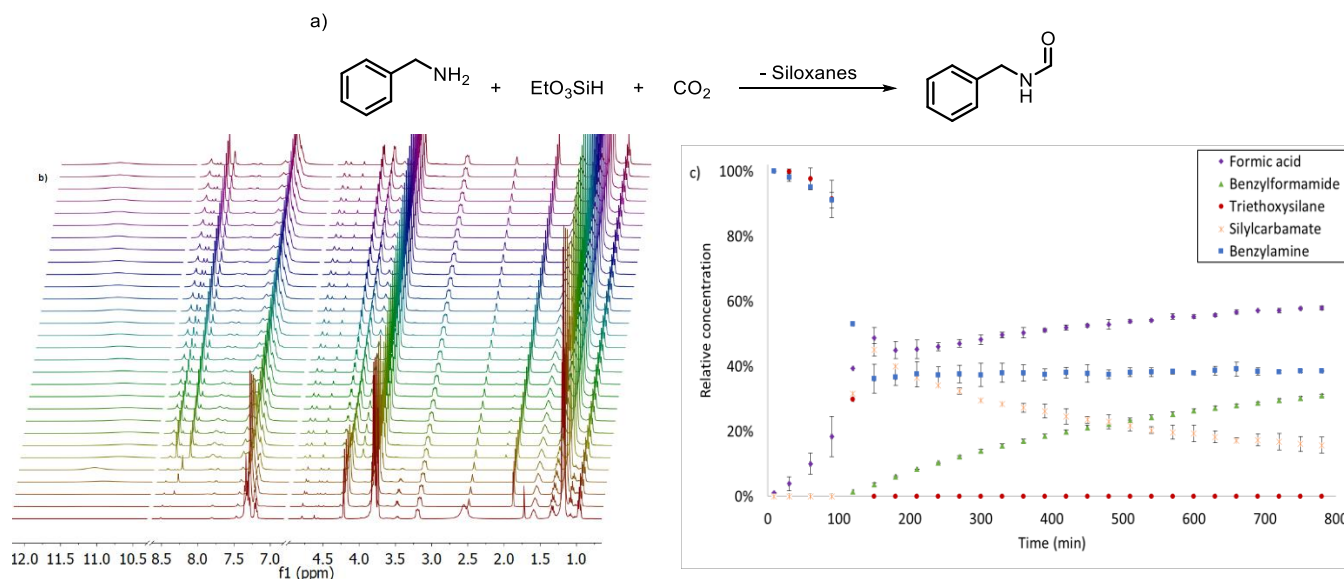


Figure 6: a) N-formylation of benzylamine with triethoxysilane. b) ^1H NMR spectra of benzylamine N-formylation with EtO_3SiH under CO_2 (20 bar) over a period of 13 h. For full spectra Figure S58. c) Kinetic curves for the N-formylation of benzylamine with triethoxysilane and CO_2 . Reaction conditions: triethoxysilane (0.5 mmol), benzylamine (0.5 mmol), DMSO-d_6 (0.5 ml), $[\text{TBA}][\text{OAc}]$ (10 mol%), CO_2 (20 bar), 298 K.

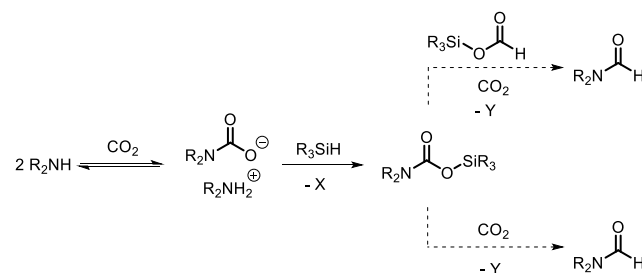
Pathway 3

Pathway 3, involving a silylcarbamate intermediate, was proposed from the N-formylation of morpholine.^{19,30} Morpholine, like some of the other anilines studied, forms a stable carbamate salt even in the absence of a base. Moreover, stabilization of the carbamate salt was demonstrated as non-essential and potentially degradatory for the N-formylation of morpholine.¹⁹ Nevertheless, base catalysts including guanidines,¹⁹ TBD,^{27,28} Cs_2CO_3 ,²⁴ or carboxylates²² catalyze the N-formylation of morpholine. However, the role of the base in pathway 3 remains unclear. Indeed, little is known about pathway 3 including the mechanism by which the silylcarbamate is formed and its subsequent transformation into the N-formylated product. Two possibilities were proposed for its transformation to the product (Scheme 6).¹⁹ One is direct and the other includes the other known formoxysilane intermediate. In both cases, CO_2 was required for the transformation to proceed in the presence of the tetramethylguanidine catalyst.¹⁹ Understanding the silylcarbamate intermediate, its formation and reactivity as well as the formoxysilane role and the reaction delay is essential to complete pathway 3. For this purpose, the reaction of benzylamine with triethoxysilane was studied, with each step of the reaction analyzed.

The reaction of benzylamine with CO_2 and triethoxysilane may be divided into three phases (Figure 6). First, the induction period; upon addition of CO_2 benzylamine is directly converted to benzylcarbamic acid, rather than the previously proposed benzylcarbamate, but then remains essentially unchanged for the next 100 minutes of the reaction. During this

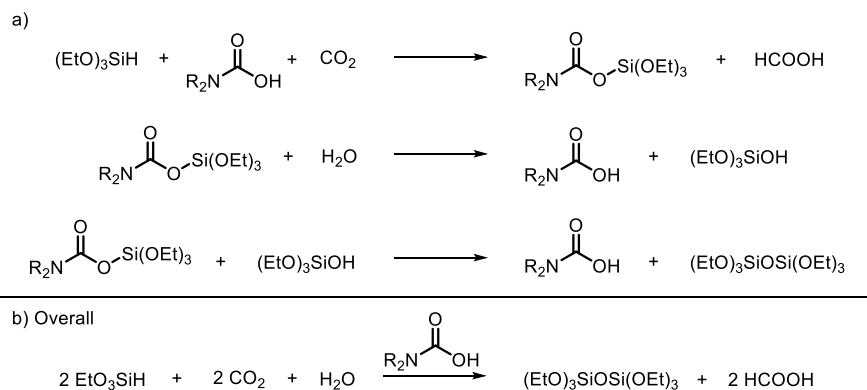
period, only 8% of the triethoxysilane reacts to form formic acid. Notably, traces of ethanol are also detected. The second phase comprises an extremely rapid reaction between triethoxysilane and benzylcarbamic acid and, within 10 minutes, all of the hydrosilane and 65% of benzylcarbamic acid are consumed. However, the N-formylated product is not observed and, instead, an intermediate identified as silylcarbamate^{19,30,47,48} appears, supporting the proposed pathway 3. Simultaneously, a large increase in the quantity of formic acid is observed. The third stage of the reaction involves the gradual conversion of the silylcarbamate to the N-benzylformamide product.

Scheme 6: Proposed transformations of silylcarbamate to N-formylated compounds along pathway 3



X and Y represent previously unreported reaction side products. Scheme adapted from reference ¹⁹.

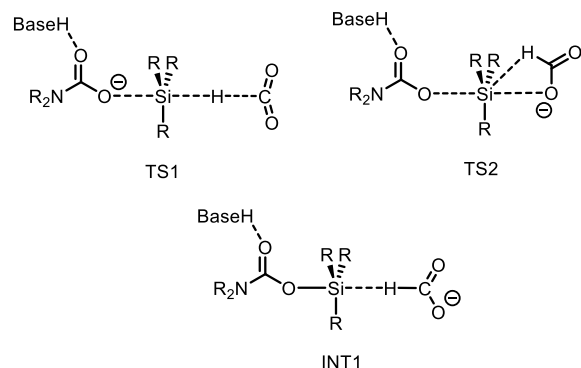
Scheme 7: Proposed reactions involved in the water induced delay to the N-formylation reaction



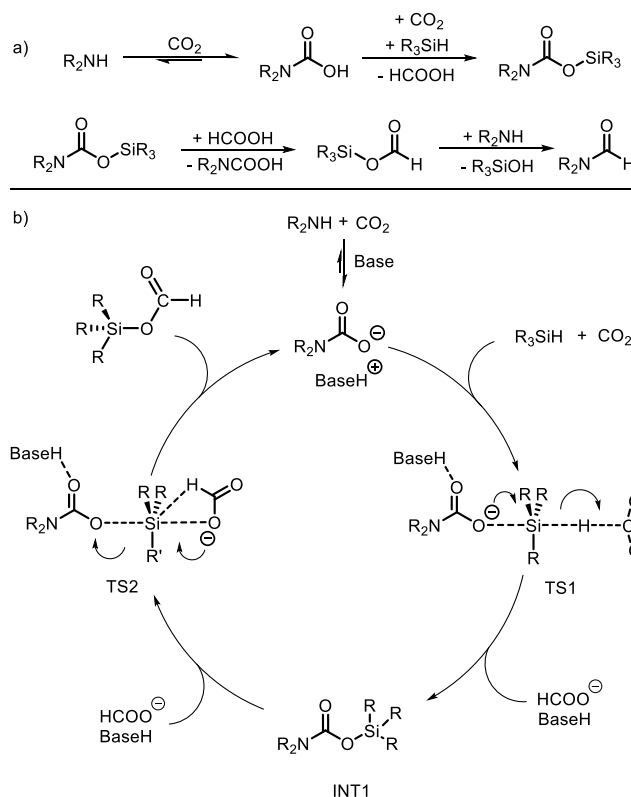
a) Proposed series of reactions responsible for benzylamine N-formylation reaction delay. b) Overall observable reaction.

The initial reaction kinetics resemble product catalyzed reactions, but upon addition of 20 mol% of benzylformanilide to the reaction mixture no changes were observed (Figures S72 and S73). Addition of formic acid slightly accelerates the reaction (Figures S74 and S75). However, the acceleration is insufficient to explain the observed 'step' change during N-formylation of benzylamine. One way in which formic acid can form in the reaction is from the hydrolysis of formoxysilane with trace water.^{38,46} Hence, we hypothesized that water causes a reaction delay, which is the opposite to product catalyzed reactions with a similar kinetic profile. Indeed, addition of trace amounts of water increases the induction time from 100 minutes to 300, slightly larger quantities to almost 400 minutes and further increases result in the slow, but complete transformation of triethoxysilane to formic acid (Figures S76 – S81). In the reaction with excess water, N-formylation was not observed and the reaction stopped after depletion of the triethoxysilane. Large quantities of water also prevent the N-formylation reaction when phenylsilane is used as the reductant. However, trace water and even quantities as large as 10 mol% do not affect the reaction kinetics¹⁹ as in the case of triethoxysilane. In the presence of the catalyst, phenylsilane rapidly reacts with water, removing it prior to reaction with CO_2 .^{49,50} As a result, trace water only decreases the initial quantity of phenylsilane in the reaction rather than causing a reaction delay.

Scheme 8: Calculated transition states and intermediates along pathway 2 for CO_2 reduction with hydrosilanes³⁵



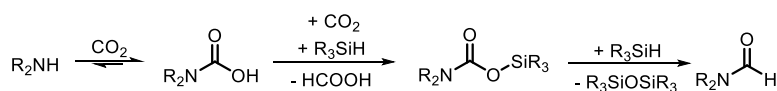
Scheme 9: Pathway 3 for the N-formylation of amines



a) Pathway 3 reaction scheme. b) Proposed mechanistic cycle for the rate determining CO_2 reduction step.

A second way in which formic acid can potentially form is from the reaction of carbamic acid with the hydrosilane and CO_2 , resulting in the simultaneous formation of the silylcarbamate. This reaction is actually observed in the second phase of the N-formylation reaction, where silylcarbamate forms along with large quantities of formic acid. However, in the presence of water silylcarbamates are readily hydrolyzed back to carbamic acids and silanols,⁵¹ which can react further with silylcarbamates to form the corresponding carbamic acids and $\text{Et}_3\text{SiOSiOEt}_3$ (Scheme 7).⁵²

Scheme 10: Proposed pathway 3' for the N-formylation of amines



Considering that carbamic acids are required for the reaction delay, it appears that the reaction of carbamic acid with hydrosilane and CO₂ followed by hydrolysis of the resulting silylcarbamate is responsible for the induction period observed during benzylamine N-formylation with triethoxysilane. Thus, when all water and silanols are consumed the desired N-formylation reaction can proceed, which is characterized by rapid consumption of triethoxysilane, benzylcarbamic acid and the concomitant formation of formoxysilanes and silylcarbamates.

The reactions are accompanied by characteristic substituent exchange around the silicon center identified by the presence of ethanol in the initial phases of the reaction and confirmed by EXSY NMR experiments as well as the detection of tetraethoxysilane (Figure S64). Hence, similar five-membered TSs are expected for pathway 3 en-route to silylcarbamate as for pathway 2 towards formoxysilanes. In the presence of an amine, two such TSs as well as one high energy intermediate were proposed by DFT calculations during formoxysilane formation (Scheme 8).³⁵ Moreover, the intermediate strongly resembles the silylcarbamate observed during the N-formylation of benzylamine. The only difference is incomplete elimination of formate/formic acid from the intermediate. However, formic acid is also observed during the N-formylation of benzylamine. Hence, it appears that stabilization of the carbamate (R₂NCOO⁻) with basic amines results in the complete transformation of this calculated intermediate to the experimentally observed silylcarbamate and formic acid. The silylcarbamates then react with formic acid to form formoxysilane(s). Hence, almost the same mechanism can be proposed for pathway 3 as for pathway 2 (Scheme 9). The observed difference between pathway 2 and 3 is dependent on the relative stabilities of silylcarbamates and formoxysilanes, which defines the major intermediate detected in solution. For benzylamine and morpholine it is the silylcarbamate. A mixture of silylcarbamates and formoxysilanes is formed with p-substituted anilines. Finally, in the case of N-methylaniline only formoxysilanes are detected. Nevertheless, the pathways do not seem to substantially differ, at least during the reduction of CO₂, and only the most stable intermediate along the N-formylation pathway varies.

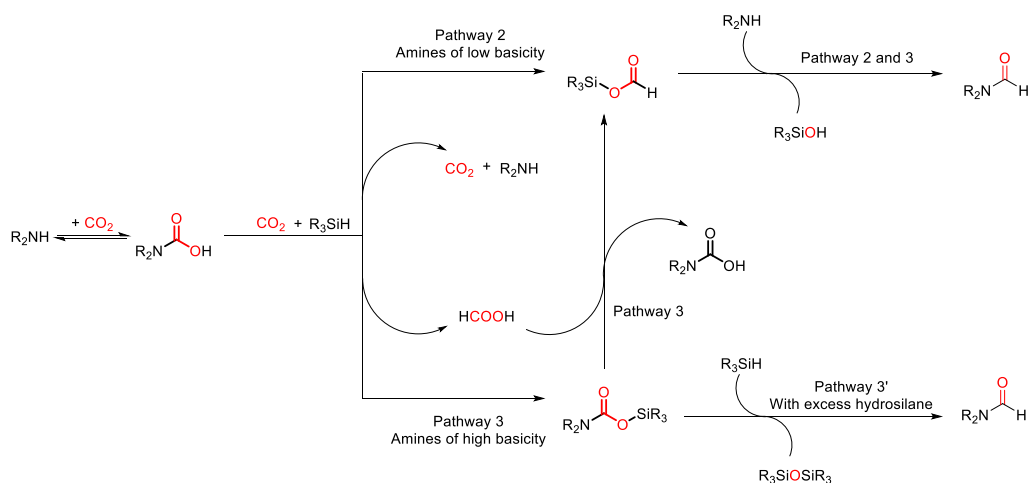
In the final stage of the reaction, benzylformamide gradually forms from the reaction of benzylamine with formoxysilane. However, the rate of the reaction is dependant on the stability of the silylcarbamate, which hinders formoxysilane formation. Overall, benzylamine N-formylation with triethoxysilane proceeds at comparable rate to the N-formylation of N-methylaniline. Nevertheless, with phenylsilane, N-formylation of benzylamine is ~3.3 times faster (Figures S84 - 85). The effect

of the hydrosilane on the reaction rate is usually assigned to the SN₂-type TS formed during reduction of CO₂ and, hence, steric hindrance around the silicon center.²⁶ However, phenylsilane also has three Si-H bonds, which can act as a hydride source, whereas triethoxysilane only has one. In effect, with phenylsilane an excess of reducing agent is normally used. Similarly, excess of triethoxysilane results in the complete N-formylation of benzylamine within 4 hours in comparison to incomplete reaction after 13 hours with only one equivalent of the hydrosilane (Figure S82 - S83). Five equivalents of triethoxysilane were used for the experiment, rather than three, in order to compensate for the formation of formoxysilane. Surprisingly, the excess triethoxysilane only slightly decreases the initial reaction delay to 60 minutes and does not affect the rate of silylcarbamate formation. However, the excess hydrosilane strongly affects the rate of the transformation of the silylcarbamate to the N-formylated product.

Direct conversion of silylcarbamates to the product has been proposed.^{19,30} In addition, silylcarbamate cleavage with chlorosilanes to siloxanes and isocyanates is known.⁵¹ The formation of siloxanes also appears as the final reaction by-product of the N-formylation reaction, which suggests that direct reduction of silylcarbamates with excess hydrosilane to N-formylated compounds and siloxanes is possible. In the absence of excess hydrosilane the silylcarbamate is gradually converted to formoxysilane leading to the slow formation of the N-formylated product. Whereas in the presence of excess hydrosilane, the silylcarbamate is directly reduced to the formamide, which corresponds to pathway 3' (Scheme 10).

Thus, pathway 2 and 3 share the same mechanism for the CO₂ reduction step, but differ according to the relative stabilities of the silylcarbamate and formoxysilane intermediates, which defines the major intermediate observed in solution. Due to the low stability of the carbamate linkage (NCOO⁻) with N-methylaniline, no silylcarbamates are observed and only formoxysilanes are detected. However, as the stability of carbamate increases, silylcarbamate formation becomes gradually favored until it becomes the dominant species in solution. A mixture of silylcarbamates and formoxysilanes is observed in-between the two extreme cases. The N-formylated product forms by gradual conversion of silylcarbamate to formoxysilane, which then reacts with the amine to form the desired product. Formate or formic acid is required for silylcarbamate transformation to formoxysilane rather than CO₂ as previously proposed.¹⁹ Nevertheless, in the presence of excess hydrosilane the silylcarbamate can be directly reduced to the final N-formylated product without the need for formoxysilane formation (Scheme 11).

Scheme 11: Overview of N-formylation reaction pathways in relation to the conditions



Formoxysilane and silylcarbamate side reactions with silanols are not shown for clarity.

Conclusions

Three possible pathways have been proposed for the N-formylation of amines with CO_2 and hydrosilanes. Pathway 1, based on the direct insertion of CO_2 into the hydrosilane, was demonstrated to only operate for the N-formylation of low basicity amines in the absence of a catalyst. However, in the presence of a base catalyst, N-formylation of N-methylaniline follows pathway 2, where base stabilized carbamate salts activate the hydrosilane prior to CO_2 insertion. Some evidence suggests that direct hydrosilane activation with nucleophilic base catalysts simultaneously takes place. However, as the basicity of the amine and the related carbamate stability increases, pathway 1 is overshadowed by pathway 2, which in turn is overtaken by pathway 3 in the case of highly basic amines such as morpholine or benzylamine.

Pathway 3 appears to follow a similar CO_2 reduction mechanism as pathway 2, but with increased stability of the carbamate linkage (NCOO^-). As a result, stable silylcarbamates are observed en-route to formoxysilanes and are detected in solution instead (or together) with formoxysilanes. The final N-formylated compounds form either from the reaction of the amine with formoxysilane or by the direct reduction of the silylcarbamates with excess hydrosilane (pathway 3'). Consequently, the N-formylation pathway is dependent on the amine and the quantity of hydrosilane present. It is likely that the substrate dependency might also explain the discrepancy in proposed pathways towards N-methylamines and amins, which in the first step also originate from the reduction of CO_2 to formoxysilanes, but may vary according to the stability of the silylcarbamate.

For all CO_2 reduction reactions with hydrosilanes, substituent exchange is observed around the silicon center of the hydrosilane supporting the formation of a five-membered hypervalent silicon species during the reaction, either as an intermediate or, more likely, as an SN_2 -type transition state.³⁵ Silanols, the primary reaction by-products, further react with the formoxysilane intermediates resulting in formic acid and siloxanes and an amine:hydrosilane (Si-H bond) ratio of at least 1 : 2 is required. The ratio needed increases in the presence of

water, which hydrolyses the formoxysilanes to silanols, siloxanes and formic acid. In the case of silylcarbamate, water induces a reaction delay as the silylcarbamate intermediate undergoes hydrolysis back to the starting carbamate and silanols, which further hinder the reaction. However, as phenylsilane is the most commonly used hydrosilane the amine to Si-H ratio is automatically augmented to 1 : 3 resulting in little significance of water induced side reactions.

Finally, this study demonstrates that organic and salt N-formylation catalysts act as bases rather than nucleophiles. A general base-catalyzed mechanism indicates that a large number of bases will be catalytically active for the reaction. It is our hope that these findings will facilitate the search for optimal base catalysts and the development of even more efficient N-formylation reaction with CO_2 .

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Notes

The authors declare no competing financial interests.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and NMR spectra.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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