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Autocatalytic *O*-Formylation of Alcohols Using CO_2

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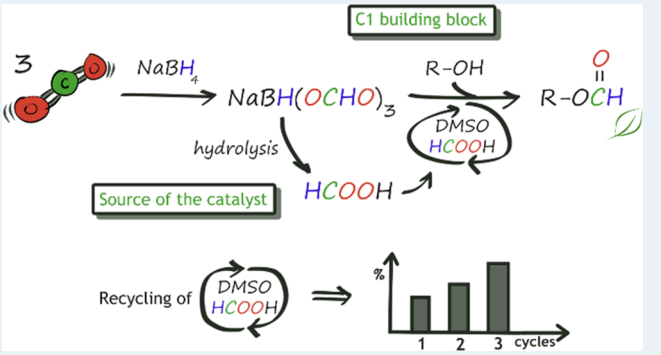
ABSTRACT: Global drive away from fossil feedstock requires the development of synthetic procedures to enhance the efficiency of CO_2 capture and utilization processes using renewable starting materials and catalysts. Here, we report an alternative reaction pathway for the *O*-formylation of alcohols and bio-alcohols, which affords industrially relevant formate esters. Most products, reported herein, derive their carbon atoms exclusively from renewable sources. The reaction is catalyzed by formic acid, which can also be produced directly from CO_2 captured in the reaction. The resulting in situ produced formic acid improves the reaction rate, with each catalyst recycling by simple filtration, product distillation, and reuse of the residual reaction mixture. Hence, CO_2 is used as a C1 building block and simultaneously reduced to formic acid, which in turn autocatalytically promotes the reaction.



KEYWORDS: *autocatalysis, organocatalysis, CO_2 utilization, reduction, O-formylation*

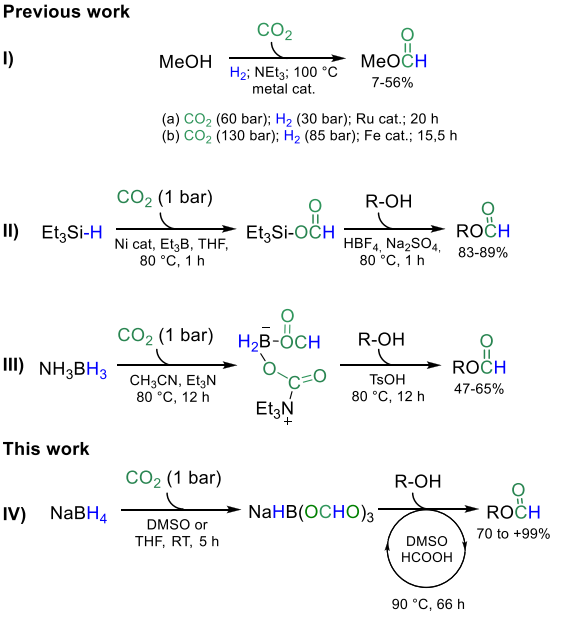
INTRODUCTION

Carbon capture and utilization (CCU) has emerged as a promising strategy for mitigating anthropogenic CO_2 emissions.[1] In this context, CO_2 has been extensively explored as a renewable C1 building block in the synthesis of fine chemicals, fuels, and polymers.[2−11] More recently, however, CO_2 has also been applied as a promoter, facilitating chemical reactions.[12] Therefore, combining these two complementary strategies, that is, using CO_2 as both C1 and catalyst source,[13] could further develop CO_2-based chemistry.

In the synthesis of fine chemicals, numerous homogeneous metal and non-metal catalysts have been tested in combination with dihydrogen,[14,15] boranes,[16−18] and hydrosilanes[19−21] as the accompanying CO_2-reducing agents. Surprisingly, though, sodium borohydride ($NaBH_4$) has only been used as a CO_2 reductant for the *N*-formylation[22] and *N*-methylation[23] of amines, which are the most widely explored reductive coupling reactions of CO_2.[20,24−26] Notably, $NaBH_4$ is an industrially applied reducing agent[27] that can reduce CO_2 in the absence of catalysts[28−30] and may be used in wet media. Moreover, $NaBH_4$ can be regenerated from reaction byproducts at the end of a process, thereby allowing circular use of $NaBH_4$ via recycling of undesirable reaction waste.[31−33] Therefore, the synthesis of fine chemicals incorporating $NaBH_4$ should be further explored toward producing sustainable compounds.

As with the synthesis of fine chemicals using $NaBH_4$, *O*-formylation reactions of alcohols using CO_2 as C1 source, irrespective of reducing agent, have also been mostly overlooked in the literature (Scheme 1, strategies I−III). Attempts to implement *N*-formylation protocols for the *O*-

Scheme 1. Previous Strategies Described for the *O*-Formylation of Alcohols using CO_2 and the Approach used in this Work



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formylation of alcohols have either failed or required further additives.[34,35] Instead, formate esters are usually prepared through esterification of primary alcohols with formic acid or through the reaction of alkyl halides with formamide,[36] although lipases have also been used in transesterification reactions for the same purpose.[37] Nevertheless, the resulting formate esters are valuable compounds as flavors and fragrances[38,39] and also stand out as organic phases in biphasic (liquid−liquid) systems in oxidoreductase biocatalysis[40−42] and as protective groups frequently used in organic chemistry.[43] For these reasons, the potential of CO_2 for *O*-formylation reactions remains untapped, especially in green chemistry.

O-formylation of methanol using CO_2 and Ru-based catalysts in the presence of NEt_3 has been described (Scheme 1, Ia),[44] and the same reaction with Fe-based complexes has also been reported previously (Scheme 1, Ib).[45] Through these processes, H_2 can be used as the reductant, albeit affording methyl formate in only moderate yields. However, good yields of formate esters were reached in Ni-catalyzed hydrosilylation of CO_2 followed by *O*-formylation of alcohols with silyl formates in the presence of HBF_4 (Scheme 1, II).[35] More recently, following a metal-free approach using ammonia borane in acetonitrile, the generated boryl formate was subsequently used as a carbon source in the *O*-formylation of benzylic alcohols catalyzed by TsOH, producing formate esters in moderate-to-good yields (Scheme 1, III).[46] The presence of stable silyl and boryl formates indicates that the *O*-formylation step proceeds via a transesterification reaction. We therefore hypothesized that this reaction can be acid catalyzed using triformatoborohydride as the *O*-formylating reagent and formic acid as the catalyst.

Considering the above, we aimed at using triformato borohydride, formed in the reaction of $NaBH_4$ with CO_2,[28] as an efficient *O*-formylating agent and as a source of formic acid to efficiently catalyze the *O*-formylation reaction. In this study, we observed that in situ formation of formic acid results in an autocatalytic process, wherein reaction rates improve in each recycling cycle (Scheme 1, IV). For bio-derived alcohols, all carbon atoms in the product are derived from renewable sources, thereby eliminating the need for any fossil-based feedstock in the synthesis of industrially relevant formate esters while simultaneously using CO_2 as a C1 source.

RESULTS AND DISCUSSION

Formic acid was synthesized by CO_2 reduction with sodium borohydride[47] followed by hydrolysis of sodium triformato borohydride at room temperature (Scheme 2 and SI). After optimizing the reaction conditions, we obtained 2.86 equivalents of formic acid per equivalent of precursor, nearly doubling the previously reported yield of only 1.5 equivalents.[28] This result demonstrates that three molecules of CO_2 can be captured and quantitatively reduced to formic acid at room temperature with $NaBH_4$.

$NaBH(OCHO)_3$ was also tested for *O*-formylation of alcohols using a solution of $NaBH(OCHO)_3$ in DMSO (approximately 0.95 M) and benzyl alcohol as a model substrate (Table 1). The initial reaction conditions were set according to reported procedures for the *N*-formylation of amines with the same formylating agent.[47] DMSO was selected as the reaction solvent due to its ability to simultaneously solubilize $NaBH_4$, $NaBH(OCHO)_3$, and the reaction substrate(s), which was less efficient with other solvents (SI) and its comparatively high safety and low environmental impact among alternative dipolar aprotic solvents.[48,49] After 18 h at 70 °C, the reaction afforded the desired benzyl formate in 5% yield (Table 1, entry 1), as expected because alcohols are less nucleophilic than amines and *N*-formylation protocols are difficult to transfer to *O*-formylation of alcohols.

Scheme 2. Synthesis of Formic Acid from CO_2 and Sodium Borohydride via Sodium Triformatoborohydride

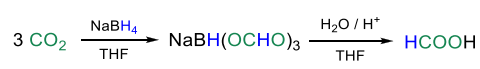

Table 1. Optimization of *O*-Formylation Using Triformatoborohydride

entry[a]	$NaBH(OCHO)_3$ (eq.)	*T* (°C)	FA (eq.)	yield
1	1.3	70		5
2	1.3	90		20
3	1.3	90	0.5	34
4	1.3	90	1.0	47
5	1.3	90	1.5	57
6	1.3	90	2.0	63
7[b]	1.3	90	2.0	78
7[c]		90	2.0	5

[a]Reaction conditions: 1 mL 0.95 M solution of $NaBH(OCHO)_3$ in DMSO, 0.75 mmol benzyl alcohol, 18 h reaction time. Further details are provided in the SI. [b]66 h. [c]An equivalent volume of DMSO was added instead of triformatoborohydride solution.

Increasing the reaction temperature to 90 °C only modestly improved the yield to 20% (Table 1, entry 2). However, adding gradually increasing amounts of formic acid (Table 1, entries 3−6) substantially improved the efficiency of the reaction with 2 equivalents of formic acid, resulting in benzyl formate in 63% yield after 18 h (Table 1, entry 6) and 78% yield after 66 h (Table 1, entry 7). Further increase in the amount of added formic acid confirmed the observed reactivity trend, where the more acidic environment resulted in a higher reaction rate. Alternatively, the use of less formic acid and longer reaction times yields the same quantity of product (SI). A blank test with two equivalents of formic acid in the absence of $NaBH(OCHO)_3$ produced benzyl formate in only 5% yield (Table 1, entry 8), indicating that formic acid predominantly acts as the reaction catalyst rather than a formylating agent on its own.

From a catalytic perspective, the large amount of formic acid required to quickly reach high yields may appear discouraging. Nevertheless, formic acid is inexpensive (700 to 900 USD per metric ton),[1] widely available (annual production of >870 kt), and sustainable when sourced from CO_2. Moreover, formic acid can be easily recycled, as shown below.

Using two equivalents of formic acid and under the optimized reaction conditions, we explored the substrate scope (Scheme 3). Aliphatic primary alcohols provided the best reactivity, affording the desired products in excellent yields surpassing 88% (**2a−2d** and **2j**), with methanol even reaching >100% yield (**2a**). The excess methyl formate produced by *O*-formylation of methanol is a side product of the *O*-formylation reaction. Indeed, methyl formate was observed in all reactions irrespective of substrate (vide infra). With secondary aliphatic alcohols, the product yields were slightly lower, i.e., 75−82%,

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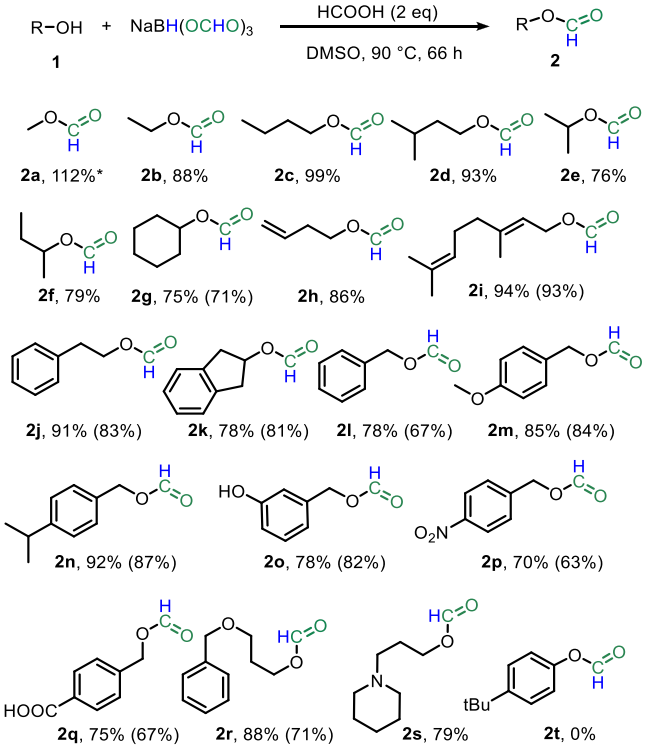
Scheme 3. Reaction Scope Performed under Optimized Reaction Conditions[a]



[a]Reaction conditions: 1.2 mL of 0.95 M $NaBH(OCHO)_3$ solution in DMSO, alcohol (0.9 mmol), 66 h at 90 °C. Product yields were quantified from crude reaction mixtures by ^1H NMR spectroscopy using mesytilene as an internal standard. Yields in parenthesis are isolated yields obtained as described in the SI. Isolated yields were not determined for volatile compounds **2a**−**2f** and **2h** due to volatility issues and neither for **2s** due to its instability. Methanol was formed as a side product in the reaction, which resulted in yields above 100% (vide infra). With the exception of methyl formate (**2b**), the reported yields correspond to conversions. The sum of unreacted starting material and product correspond to 100% mass balance of the reactions.

most likely due to the higher steric hindrance of the substrates (**2e**−**2g** and **2 k**).

Benzylic and allylic alcohols were also efficiently transformed into the corresponding formate esters (**2i** and **2m**). In addition, the *O*-formylation protocol was compatible with different functionalities, including alkene (**2h** and **2i**), aryl (**2j**, **2k**, and **2 m**), phenol (**2o**), nitro (**2p**), ether (**2n** and **2r**), carboxylic acid (**2q**), and tertiary amine (**2s**) groups. Mass balance calculations were used to confirm that side products did not form in the reactions, and consequently, it can be seen that this procedure is selective even in the presence of other reducible functional groups.

The general reactivity trends show that electron-withdrawing groups slightly decrease the yield, whereas electron-donating groups enhance the yield reflecting the alcohols' nucleophilicity. In line with the hypothesis, attempts to *O*-formylate 4-*tert*-butylphenol (**2t**), the alcohol with the lowest nucleophilicity in the substrate scope, were unsuccessful. Because compounds **2a**−**2f** and **2i** are bio-produced alcohols, the reaction products are entirely renewable. Furthermore, scaling the reaction of geraniol (**2i**) to 1 g did not affect the yield of geranyl formate as an isolated yield of 93% was obtained (SI).

Mechanistic Studies. To gain insights into the role of formic acid in the reaction in operando NMR spectroscopy and ^{13}C labeling, experiments were performed with and without HCOOH (Figure 1). The in operando NMR

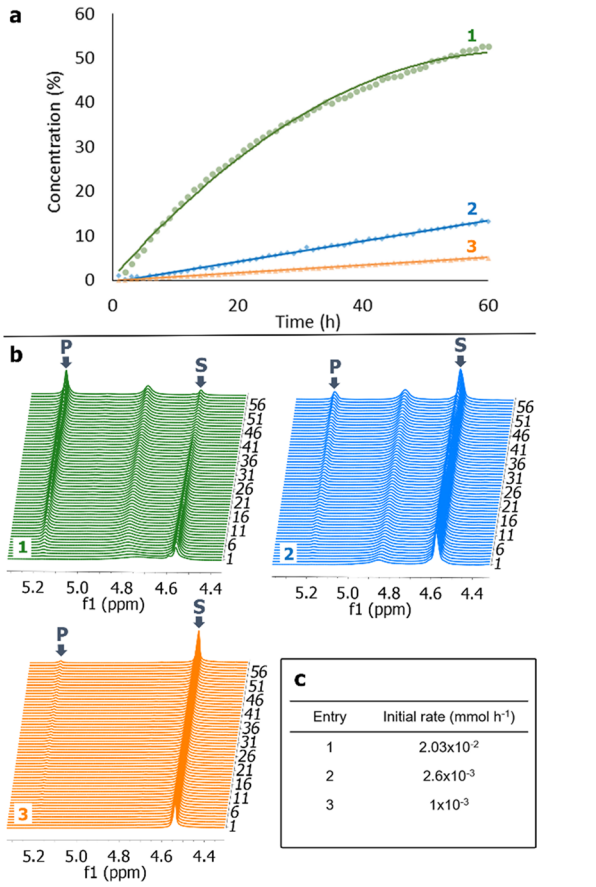


Figure 1. (a) Variation of concentration as a function of time for the *O*-formylation of benzyl alcohol to benzyl formate under the following conditions: (1) $NaBH(OCHO)_3$ and 2.5 equivalents of formic acid (green), (2) $NaBH(OCHO)_3$ only (blue), (3) 2.5 equivalents of formic acid only (orange). Product yields were determined using mesitylene as an internal standard. (b) In operando ^1H NMR spectra under the aforementioned conditions. The peaks at 5.2 ppm correspond to the -CH_2-OCHO group signal indicative of the formation of benzyl formate (P). The peaks at 4.55 ppm assigned to the -CH_2-OH group correspond to the substrate (S), whereas the peaks at 4.8 may be attributed to a reaction intermediate. (c) Initial rates of benzyl alcohol *O*-formylation calculated from in operando ^1H NMR spectroscopy; these calculations were performed using the slope of the curve concentration vs time during the first 10% conversion interval (see more details in the SI).

spectroscopic studies confirmed that formic acid primarily does not act as the formylating agent in the reaction as only 5% of benzyl alcohol was formylated over 60 h (Figure 1, orange curve). The reaction with triformato borohydride in the absence of formic acid also resulted in a low benzyl formate yield of 15% after the same reaction time (Figure 1, blue curve). Conversely, adding formic acid markedly enhanced the initial reaction rate by almost 8-fold (Figure 1c), which confirmed that formic acid acts as the reaction catalyst, as observed in the reaction screening. Interestingly, multiple formate (-CHO-) signals between 8.0 and 8.5 ppm, which could not be attributed to triformato borohydride or formic

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acid alone, were observed in the initial ^{1}H NMR spectra prior to product formation (Figure S1a). The gradual shift of a peak at 8.1 to 8.2 ppm attributed to the -CHO- proton and that of a peak at 12.5 to 13.0 ppm corresponding to an acidic proton indicate that the exchange between triformatoborohydride and formic acid does occur under such reaction conditions.

Labeling experiments with $^{13}CO_2$ confirmed that all three formyl groups in $NaBH(O^{13}CHO)_3$ originated from $^{13}CO_2$ (SI). In contrast, in the presence of two equivalents of unlabeled formic acid, only 57% of the resulting benzyl formate was labeled with ^{13}C. The complementary experiment between unlabeled $NaBH(OCHO)_3$ and $H^{13}COOH$ led to the same result (SI). The ratio of ^{13}C-labeled formate groups in the reaction also reflected the ratio of labeled product.

In the initial stages of the reaction, *O*-formylation of benzyl alcohol is also accompanied by simultaneous reduction of formate, either from HCOOH or triformatoborohydride, to methanol (Scheme 4), as shown by the disappearance of the hydride signal of $NaBH(OCHO)_3$ in the ^{1}H NMR spectrum at 3.8 ppm and appearance of a new methanol signal at 3.16 ppm. Methanol is then *O*-formylated in a side reaction to methyl formate marked by peaks at 3.65 and 8.15 ppm in the in operando NMR spectra (SI). Therefore, sodium triformatoborohydride is the *O*-formylating reagent only at the beginning of the reaction (initial, ~6 h), during which it is also gradually converted to $B(OH)_n(OCHO)_{3-n}$, sodium formate, and their Lewis acid−base adduct, i.e., $NaB(OH)_n(OCHO)_{4-n}$ (Scheme 4).

Scheme 4. Reduction of Formate to Methanol and Lewis Acid−Base Equilibrium between Sodium Formate and Diformatoboronic Acid[a]

$$NaBH(OCHO)_3 + HCOOH \longrightarrow B(OH)_n(OCHO)_{3-n} + NaOCHO + 1/2\ MeOH$$

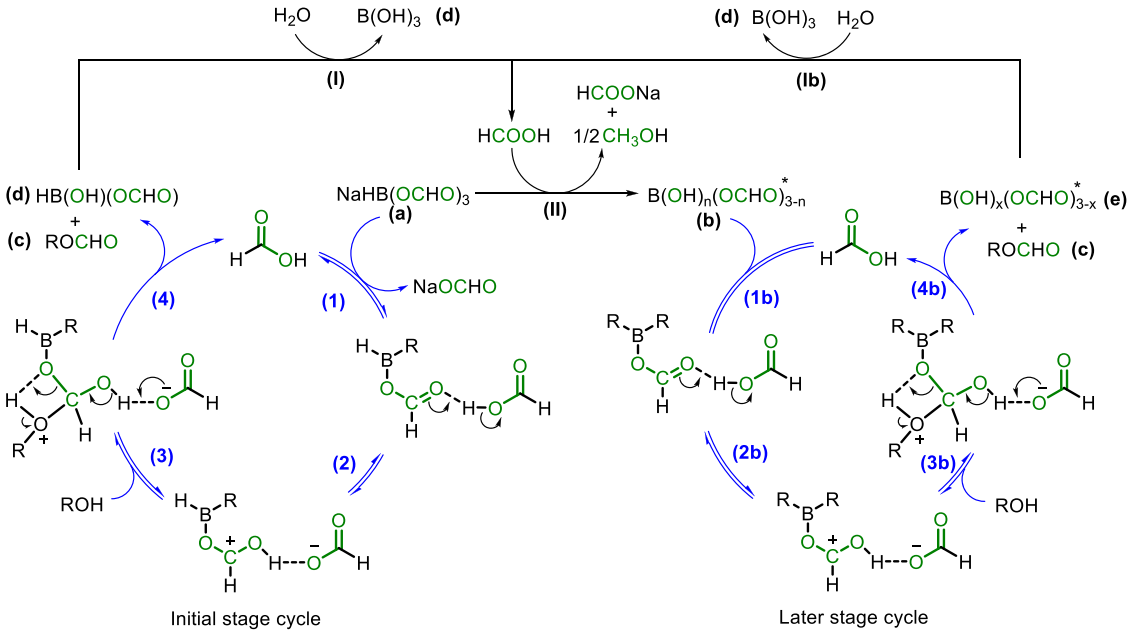
$$B(OH)_n(OCHO)_{3-n} + NaOCHO \rightleftharpoons NaB(OH)_n(OCHO)_{4-n}$$

[a]Due to chemical exchange in the system, the quantities of formate and acid groups on the boron center may vary (n = 0, 1, or 2).

In later stages of the reaction, $B(OH)_n(OCHO)_{3-n}$, sodium formate or their Lewis acid−base adduct acts as the *O*-formylating reagent. If sodium formate or $NaB(OH)_n(OCHO)_{4-n}$ were the formylating reagents, the addition of sodium formate to the reaction would accelerate product formation either through direct *O*-formylation or through changes in the reaction equilibrium (Scheme 4). However, adding sodium formate delayed the reaction, indicating that formato boranes $B(OH)_n(OCHO)_{3-n}$ become the *O*-formylating reagents in the system once triformato borohydride is consumed (SI). The presence of $B(OH)_n(OCHO)_{3-n}$ species was determined by mass spectrometry analysis (SI). Obtained LC−MS spectra were consistent with two of these structures, $(HO)B(OCHO)_2$ and $(HO)_2BOCHO$, respectively.

Two almost identical catalytic cycles may be proposed for the *O*-formylation reaction (Scheme 5): One for the initial stage of the reaction, where triformato borohydride (a) is the *O*-formylation reagent, and another for later stages of the reaction, where a mixture of formato boranes (b) acts as the *O*-formylation reagents. In the presence of formic acid, the *O*-formylation reaction itself with either triformato borohydride (a) or formato boranes (b) may be considered as a type of acid-catalyzed (trans)esterification reaction, which is supported by the use of acetic acid instead of formic acid, which also catalyzes the reaction albeit less efficiently than formic acid (SI). In the initial stages of the reaction, triformato borohydride (a) and, in the later stages, formato boranes (b) are activated by proton transfer from formic acid (Scheme 5, step 1−2 and 1b−2b), which promotes nucleophilic attack by an alcohol (Scheme 5, step 3 and 3b) and accompanies formate transfer to the alcohol that generates the desired *O*-formylated product (c) (Scheme 5, step 4 and 4b). Hydroxy boranes (d and e) (Scheme 5) are produced as reaction by-products, as identified by ^{11}B NMR spectroscopy (SI). The

Scheme 5. Proposed Reaction Mechanism for Formic Acid-Catalyzed *O*-Formylation[a]



[a]Due to chemical exchange in the system, the quantities of formate and acid groups on the boron center vary (n = 0, 1, or 2 and x = 1 or 2).

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hydroxyl boranes (d and e) can either enter the *O*-formylation cycle as *O*-formylating reagents or they can be hydrolyzed by trace water in the system (Scheme 5, step I and Ib) to formic acid, boric acid, further hydroxyl boranes (B-$(OH)_x(OCHO)_{3-x}$), and their adducts with sodium formate as the final reaction by-products. This generation of formic acid is evidenced by the fact that more formic acid is present at the end of the reaction than the initial amount added (SI), hence making this process an autocatalytic one.

In a simultaneous side reaction that occurs in the initial stages of the reaction, triformato borohydride reacts with formic acid, producing formato boranes (b) (Scheme 5, step II) and releasing sodium formate and methanol, as determined by in operando NMR spectroscopy (Scheme 5, step II). Formato boranes (b) then enter the later-stage *O*-formylation cycle as *O*-formylation reagents, and formic acid consumed in this reaction is regenerated by partial hydrolysis of hydroxyl boranes (d and e) as mentioned.

Batch Recycling. Although some formic acid is consumed during side reactions to form methanol and, subsequently, methyl formate (Schemes 4 and 5), formic acid is also (re-)generated in the system (Scheme 5, step I and Ib, confirmed by NMR spectroscopy). Furthermore, the quantity of HCOOH at the end of the reaction is higher than that at the initial stage, which indicates that the quantity of available catalyst for each subsequent run during recycling should increase (SI). The reaction by-products (boric acid, hydroxyborane derivatives, and their sodium salts) precipitate from the reaction mixture and can be easily removed by filtration, which allows their separation and recycling to regenerate $NaBH_4$.[31−33] Produced short-chain alkyl formates can be purified by distillation, and less volatile formates can be extracted with diethyl ether. Hence, after filtration and separation of the desired product, the remaining crude reaction mixture can be reused for a new cycle by simply adding a substrate and $NaBH(OCHO)_3$.

The proposed strategy recycles not only the catalyst but also the solvent, which minimizes waste and increases the sustainability of the reaction. In addition, hydroxyborane by-products (c) can be hydrolyzed to boronic acid, which can be recycled and used to regenerate $NaBH_4$.[31,32]

Catalyst recycling following this protocol (reaction, filtration, distillation, and then addition of the substrate and the formylating agent) was performed with ethanol as the model substrate. To observe changes to the catalyst during recycling, we selected the reaction conditions (90 °C, 6 h, 1 eq of HCOOH) that produced ethyl formate in a moderate yield in the first cycle. The first, second, and third reaction cycles generated ethyl formate in 32, 38, and 48% yields, respectively (Figure 2). The increase in product yield with each run clearly demonstrates that the catalyst and solvent are easily recycled. Together with the increase in the concentration of formic acid, these findings underline the autocatalytic properties of the system, wherein more catalyst is produced during each *O*-formylating cycle.

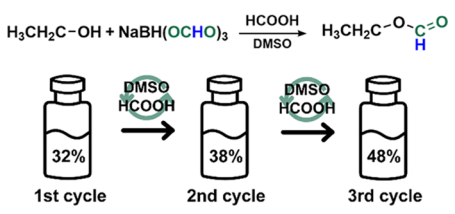

Figure 2. Recycling of the reaction batch in the *O*-formylation of ethanol to ethyl formate under conditions selected to show changes in the catalytic activity; the yield was determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

CONCLUSIONS

CO_2 can be used as both the C1 building block and source of formic acid catalyst in the *O*-formylation of alcohols, which proceeds via a $NaBH(OCHO)_3$ intermediate. $NaBH(OCHO)_3$ produces formic acid, which readily catalyzes the *O*-formylation reaction under metal-free conditions. During the reaction, the quantity of formic acid catalyst increases, resulting in an autocatalytic system wherein each cycle has a higher reaction rate than the previous. This synthetic protocol leads to fully renewably sourced compounds in good-to-excellent yields encompassing a broad scope of alcohols, including bio-based alcohols, with good functional group tolerance and high selectivity, even with substrates bearing reducible nitro, alkene, or carboxylic acid groups. This reaction can be scaled to gram quantities, and both the catalyst and reaction solvent can be recycled and reused multiple times.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.2c06218.

General experimental procedures, synthetic and analytical details of all compounds and experiments, NMR and mass spectra of the compounds in the substrate scope (Scheme 3), ^{13}C labeling experiments, in operando NMR studies, and details of catalyst recycling procedures (PDF)

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Author Contributions

P.J.D. and J.G.U. conceived and designed the project. G.G., D.S., and J.G.U. performed the experiments and data analysis. M.H., J.G.U., and G.G. discussed the results and prepared the draft. D.S. and G.G. purified the products and prepared the samples for product characterization. D.O. performed HRMS experiments. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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■ ADDITIONAL NOTE

[1]Price is for North America based on Texas commodity market range.

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