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Metal-Free Dehydrogenation of Formic Acid to $\text{H}_2$ and $\text{CO}_2$ Using Boron-Based Catalysts†

Clément Chauvier, Anis Tlili, Christophe Das Neves Gomes, Pierre Thuéry and Thibault Cantat*

Formic acid is at the crossroads of novel sustainable energy strategies because it is an efficient $\text{H}_2$ carrier. Yet, its decomposition to $\text{H}_2$ today relies on metal-based catalysts. Herein, we describe the first metal-free catalysts able to promote the dehydrogenation of formic acid. Using dialkylborane derivatives, $\text{HCOOH}$ is decomposed to $\text{H}_2$ and $\text{CO}_2$, in the presence of a base, with high selectivity. Experimental and computational results point to the involvement of bis(formyloxy)borates as key intermediates in the C–H bond activation of a formate ligand.

Introduction

Besides its utilization as a preservative and antibacterial agent in the agriculture industry, formic acid (FA) is at the crossroads of novel sustainable energy strategies. With a high energy density of 2104 Wh L$^{-1}$, FA is indeed investigated as a potential energy vector either directly as a fuel in electrochemical fuel cells or as an intermediate to the formation of methanol (4900 Wh L$^{-1}$). Additionally, FA is an attractive hydrogen carrier because of its relatively high hydrogen content (4.4 wt%) and “hydrogen batteries” have been proposed, which rely on the reversible hydrogenation of $\text{CO}_2$ and dehydrogenation of formic acid, in basic media, for $\text{H}_2$ storage. Importantly, efficient catalysts are required to promote the rapid and selective dehydrogenation of FA to $\text{CO}_2$ and molecular $\text{H}_2$ and their design has been the focus of many efforts within the last two decades. While early studies focused on the development of ruthenium and iridium complexes, the current state of the art now also includes efficient iron catalysts and the search for noble-metal free catalysts is an active research field. Notably, Berben et al. have disclosed in 2014, that molecular aluminium-based complexes with the bis(imino)pyridine ligand promote the selective dehydrogenation of formic acid in the presence of triethylamine with TOFs up to 5200 h$^{-1}$. More recently, Maschmeyer et al. have shown that sodium germanate heterogeneously promotes $\text{H}_2$ formation from formic acid vapors at 300 $^\circ$C. So far, a metal-free catalyst able to convert $\text{HCOOH}$ to $\text{H}_2$ and $\text{CO}_2$ has yet remained elusive. The main challenge of this endeavour lies in the necessity of a double, antagonistic, activation of formic acid. First, the acidic O–H proton must be abstracted with the aid of a Brønsted base to yield a formate anion. The C–H bond cleavage then requires a Lewis-acidic species, able to promote hydride abstraction despite the presence of a strongly coordinating formate medium.

Herein we disclose that dialkylborane derivatives are unprecedented organocatalysts for the selective dehydrogenation of FA to molecular hydrogen and $\text{CO}_2$, in the presence of a basic additive. Mechanistic insights are provided based on experimental observations and DFT calculations and they highlight the role of bis(formyloxy)borates in this catalytic transformation.

Results and Discussion

While the deprotonation of the O–H bond in FA is easily promoted by a Bronsted base having a $\text{pK}_a > 3.7$, the activation of the C–H bond in the resulting formate anion is anticipated to be a rate limiting step and it necessitates a Lewis acid able to abstract a hydride anion and release $\text{CO}_2$. For the design of an efficient catalyst, it is thus mandatory to seek a Lewis acid able...
To interconvert a formate anion and CO$_2$, with a low activation energy and a negligible exergonicity. In this context, we have shown recently that guanidines are highly efficient organocatalysts in the hydroboration of CO$_2$ at 25 °C.$^{11}$ In particular, experimental and computational results pointed to a mechanism where adduct 1, formed from MTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene) and the stoichiometric BBN–I hydroborane, promotes the reduction of CO$_2$ to formate salt [2$,^+$, HCOO$^-$] with a modest activation barrier of 23.8 kcal mol$^{-1}$ and a nearly athermic balance ($\Delta$G = -3.0 kcal mol$^{-1}$) (Scheme 1). This result suggests that intermediate 2$^+$ could serve as a catalyst to promote the reverse transformation, namely the dehydrogenation of formate anions, and catalyze H$_2$ generation by quenching of the formed B–H linkage with HCOOH.

![Diagram](image1.png)

**Figure 1.** a) ORTEP view of 2$^+$ in [2$,^+$, I$^-$]. Displacement ellipsoids are drawn at the 50% probability level. Counterion and hydrogen atoms are omitted. b) ORTEP view of compound 5$^-$ in [TBDH$^-$, 5]. Displacement ellipsoids are drawn at the 30% probability level. TBDH$^-$ and hydrogen atoms on the BBN cycle have been removed for clarity.

Table 1. Metal-free Catalytic Dehydrogenation of 5 HCOOH / 2 NEt$_3$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Conv.</th>
<th>TON (time, h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[2$.^+$] (5.0)</td>
<td>TDF</td>
<td>26</td>
<td>5.2 (19)</td>
</tr>
<tr>
<td>2</td>
<td>BBN–I (5.0)</td>
<td>TDF</td>
<td>48</td>
<td>9.6 (19)</td>
</tr>
<tr>
<td>3</td>
<td>BBN–I (5.0)</td>
<td>CD$_2$</td>
<td>&lt; 5</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>BBN–I (5.0)</td>
<td>CD$_3$</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>BBN–I (5.0)</td>
<td>CD, OD</td>
<td>&lt; 5</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>BBN–I (5.0)</td>
<td>CD, CN</td>
<td>84</td>
<td>16.8 (19)</td>
</tr>
<tr>
<td>7</td>
<td>BBN–H (5.0)</td>
<td>CD, CN</td>
<td>52</td>
<td>10.4 (19)</td>
</tr>
<tr>
<td>8</td>
<td>[TBDH$^-$, 5] (5.0)</td>
<td>CD, CN</td>
<td>67$^b$</td>
<td>13.4 (19)</td>
</tr>
<tr>
<td>9</td>
<td>Cy$_2$B-I (10.0)</td>
<td>CD, CN</td>
<td>&gt; 99$^b$</td>
<td>10.4 (35)</td>
</tr>
<tr>
<td>10</td>
<td>Cy$_2$B-I (5.0)</td>
<td>CD, CN</td>
<td>&gt; 99</td>
<td>20 (19)</td>
</tr>
<tr>
<td>11</td>
<td>Cy$_2$B-I (1.0)</td>
<td>CD, CN</td>
<td>79</td>
<td>79 (19), 88 (23), 100 (40)</td>
</tr>
<tr>
<td>12</td>
<td>[Et$_3$NH$^+$, 6] (5.0)</td>
<td>CD, CN</td>
<td>&gt; 99$^b$</td>
<td>10 (8)</td>
</tr>
<tr>
<td>13</td>
<td>[Et$_3$NH$^+$, 6] (1.0)</td>
<td>CD, CN</td>
<td>78$^b$</td>
<td>78 (19), 94 (23), 100 (26)</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.2 mmol FA, 0.08 mmol TEA, 0.2 mL deuterated solvent. [a] Conversions determined by $^1$H NMR using mesitylene (10 µL) as an internal standard; mean values over at least 2 runs. [b] Catalyst was recovered unchanged. [c] Full conversion reached within 4.5 h.

boreniun cation stabilized by a π-donor nitrogen ligand was further confirmed by X-ray diffraction (Figure 1a). In the solid state, the boron atom adopts a trigonal planar geometry with a N–B bond length of 1.428(2) Å, close to the N–B distance found in aminoboranes, suggesting π-donation of the nitrogen atom from the guanidine.

Using 5 mol% [2$,^+$, I$^-$] as a catalyst, the dehydrogenation of $^{13}$C-labelled FA was undertaken in $d_6$-THF, at 130°C. Monitoring the reaction mixture by $^1$H and $^{13}$C NMR demonstrated the complete consumption of FA and the clean formation of H$_2$ (4.55 ppm) and $^{13}$CO$_2$ (126 ppm) as the only $^{13}$C-enriched product after 4 days. In contrast, a blank experiment, carried out in the absence of catalyst, showed no decomposition of FA under identical conditions. Nonetheless, a more careful insight into the proceedings of the catalytic reaction at shorter times revealed a lengthy initiation period, hence a lack of reproducibility (vide infra).

In order to increase both the rate and the reproducibility of the reaction, the dehydrogenation of FA was investigated in the presence of triethylamine (TEA) as an external base. The positive influence of bases on the kinetics of FA conversion to H$_2$ and CO$_2$ is indeed well established with metal catalysts.$^{5b, 9}$ To our delight, the combination of 5 mol% [2$,^+$, I$^-$] with triethylammonium formate (5 FA/2 TEA) in THF leads reproducibly to the clean formation of H$_2$ and CO$_2$ in ca. 26 % yield (± 5 %) after 19 h (Entry 1, Table 1) and >99 % yield after 45 h, while no H$_2$ evolution was observed in the absence of catalyst (see ESI). To the best of our knowledge, this result represents the first example of an organocatalytic dehydrogenation of FA.

Interestingly, in the presence of TEA, commercially available BBN–I proves to be an efficient catalyst and, within 19 h at 130 °C, it affords H$_2$ and CO$_2$ in 48 % yield from FA (Entry 2,
Table 1). In comparison, as noted above, only 26% yield is observed with 5.0 mol% [2⁺, I⁻], suggesting that the Lewis basicity of MTBD might be detrimental. Importantly, the solvent has a dramatic effect on H₂ generation with BBN–I, in the presence of TEA. Whereas no reaction occurs in non-polar solvents such as benzene or toluene (Entries 3 and 4, Table 1), 84% FA is dehydrogenated after 19 h at 130 °C in MeCN, with 5.0 mol% BBN–I (Entry 6, Table 1). Nonetheless, the catalytic system is inactive in the presence of polar and protic solvents such as methanol, presumably because of the competitive complexation of methanol to boron (Entry 5, Table 1). The reaction temperature also plays an important control on the outcome of the reaction and the yield plummets from 84 to 18% after 19 h, when the reaction temperature is lowered from 130 to 120 °C. Decreasing the temperature below 120 °C results in the complete deactivation of the catalytic system, even after prolonged time (ca. 30 h). Finally, the amount of base present in the reaction medium strongly controls the productivity and, using 5.0 mol% BBN–I, no reaction occurs in pure FA with 0.0 or 5.0 mol% MTBD, while 49% dehydrogenation is measured after 19 h with 10.0 mol% MTBD (see ESI).

Monitoring the products distribution by ¹H and ¹³C NMR reveals the formation of a common catalytic intermediate in the dehydrogenation of the ¹³C-labelled FA with 2/5 TEA when [2⁺, I⁻] or BBN–I are used as catalysts. This intermediate is the only boron species detected in solution at room temperature within the reaction mixture and it can be formulated as a bis(formyloxy)borate anion (5⁻). 5⁻ features two formate moieties characterized by a doublet at 8.41 ppm (JCH = 203 Hz) in the ¹H NMR spectrum and a ¹³C [¹H] resonance at 167 ppm. The ¹B [¹H] NMR spectrum presents a single peak at 8.98 ppm in d₅-MeCN, consistent with an electron-poor tetracoordinated boron center. In fact, 5⁻ is formed quantitatively when [2⁺, I⁻] is reacted with 2 equiv. FA and 1 equiv. TEA, at 25 °C (Eq. 2). 5⁻ can be isolated as a well-defined salt via the dehydrogenation of hydroborane BBN–H with 2 equiv. FA and a stoichiometric amount of a base, namely 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), MTBD or TEA (Eq. 3). While [Et₃NH⁺, 5⁻] is a colorless oil, [TBDH⁺, 5⁻] was isolated as a crystalline solid enabling its structure determination by X-ray diffraction (Figure 1b). [TBDH⁺, 5⁻] is the first example of a bis(formyloxy)borate characterized to date and it displays B–O and C–O bond lengths (B–O: 1.542(3) and 1.528(3) Å, C–O: 1.279(3) and 1.293(3) Å, C=O: 1.217(3) and 1.218(3) Å) similar to those encountered in anionic mono(formyloxy)borates derived from B(C₆F₅)₃[¹³] or HBAr₂[¹⁴] (Ar = 2,4,6-tris(trifluoromethyl)phenyl).

The ability of [TBDH⁺, 5⁻] to promote the decarboxylation of formate ions was further probed using this salt as a catalyst in the dehydrogenation of FA. With 5.0 mol% [TBDH⁺, 5⁻], 67% CO₂ / H₂ are produced from a 5 FA / 2 TEA mixture after 19 h at 130 °C and [Et₃NH⁺, 5⁻] could be recovered at the end of the reaction (Entry 8, Table 1) in agreement with Eq. 3, BBN–H is also catalytically active (Entry 7, Table 1).

Overall, the experimental findings gathered with BBN–I as a catalyst reveal the importance of bis(formyloxy)borate 5⁻ as a catalytically active species. R₂B–X (X = Cl, Br, I, OMe, OTf) precursors where thus screened to determine the electronic and/or steric influence of the R group on the catalytic activity. Catechol borane and pinacol borane derivatives (catB–Cl, catB–Br or pinB–OMe) are completely inactive in the dehydrogenation of FA, even in the presence of TEA (Entries 25, 26 and 27, Table S1). In contrast, dicyclohexyl borane derivatives exhibit a three-fold increase in activity, compared to the BBN system; and the quantitative dehydrogenation of 5 FA/2 TEA is achieved within only 4 h 30 at 130°C, with the BBN system; and the quantitative dehydrogenation of 5 FA/2 TEA is achieved within only 4 h 30 at 130°C, with 10 mol% Cy₂B–Cl (Entry 12 and 13, Table 1).
The pivotal role of the bis(formyloxy)borates 5 and 6 was further probed using DFT techniques (at the M06-2X/6-311+G(d,p) level of theory), so as to account for their observation throughout the catalysis (Scheme 2). In agreement with the experimental observations, 5 is found as the lowest energy species on the potential energy surface. No direct transition state (TS) could be localized to connect directly the saturated bis(formyloxy)borate 5 with CO2 and the hydridoborate intermediate 9, suggesting that the decarboxylation of 5 requires the decoordination of one formate ligand to restore a vacant orbital on the boron center. The trigonal formyloxyborane 7 is indeed engaged in an unfavorable equilibrium with 5 (ΔG = +11.1 kcal mol-1). Formation of 9 from 7, can then proceed via a β-hydride elimination (TS2), similar to ruthenium catalysts. In addition, Berben et al. proposed that aluminium complexes of the bis(imino)pyridine ligand can promote the decarboxylation of a formate ligand via a β-hydride abstraction assisted by the ancillary nitrogen ligand. Nonetheless, the corresponding activation energy of 51.9 kcal mol-1 is incompatible with the applied reaction conditions. In addition, a lower energy pathway was identified that corresponds to the direct hydride abstraction of an external formate anion by the neutral boron electrophile 7, via TS1 (26.6 kcal mol-1). This result confirms that, with a base/boron catalyst molar ratio of 1, no free formate anion is available and the decarboxylation of 7 can only proceeds via TS2, therefore inhibiting the catalytic dehydrogenation of pure FA with \([2^*, I^*]\).

Formed by decarboxylation of 7, the hydridoborate intermediate 9 lies 12.9 kcal mol-1 above the starting materials, accounting for our unsuccessful attempts to observe a B–H functionality. 9 is prone to protonolysis and two different pathways have been unveiled computationally for the dehydrogenation of FA with 9. H2 release by quenching of the B–H group with an external molecule of FA proceeds via TS4, with an activation barrier of 15.9 kcal mol-1 from 9. Interestingly, a pathway involving the displacement of the formate ligand in 9 by HCOOH and subsequent intramolecular dehydrogenation (via TS3) cannot be ruled out, as it involves a low activation barrier of 18.7 kcal mol-1 from 9. The dehydrogenation step reforms 7, which is ultimately converted to the more stable borate 5. Overall, the decomposition of FA involves two steps, namely the decarboxylation of a trigonal boron formate intermediate (via TS1, 26.6 kcal mol-1) and the subsequent deprotonation of FA by the reactive hydridoborate intermediate (via TS3 or TS4, 31.6 and 28.8 kcal mol-1, respectively) (Scheme 2). Both steps thus have similar energy demands and no rate determining step (RDS) can be unequivocally proposed. Nevertheless the consistency of the latter barriers with regard to the applied reaction conditions was further established using the energetic span model. With an energetic span of δE = 28.8 kcal mol-1, the calculated TOF at 130°C (403 K) is 1.0 h-1 in the same order of magnitude that experimental TOF (0.6–0.9 h-1 from Table 1, Entries 6, 7 and 8).

The influence of replacing the BBN scaffold with Cy2B or catB backbones has been investigated computationally (Schemes S2 and S3). TS1, TS3 and TS4 are very close in energy for the catalytically active BBN and Cy2B systems and the mechanistic model does not account for the greater catalytic activity of Cy2B–I. Nonetheless, the energy surface is significantly modified when catecholborane derivatives are used as catalysts (Scheme S3). Indeed, the coordination of the π-donor catecholate ligand to the boron atom significantly lowers the
electrophilicity of the catalyst and hampers the activation of the C–H bond by hydride abstraction, which necessitates an activation energy of 38.8 kcal mol⁻¹. Finally, the mechanism depicted in Scheme 2 also stresses that a bis(formyloxy)borate species (such as 5° or 6°) is the resting state of the catalyst and must dissociate to a catalytically active trigonal formyloxyboron intermediate. As a consequence, a highly electrophilic borane derivative might prevent the generation of the active species; and, experimentally, the potent electrophile BCl₃ was found inactive in the dehydrogenation of 5 FA/2 TEA, even after 48 h at 130°C (Entry 28, Table S1). This result suggests that the catalyst should bear at least two formate ions to balance the electrophilicity of the boron catalyst. In that respect, BCl₃ enables the slow dehydrogenation of formic acid with a TON of 9 and a TOF of 0.5 h⁻¹, after 19 h at 130°C (Entry 31, Table S1).

Conclusions
In conclusion, the first organocatalysts able to promote the dehydrogenation of formic acid have been unveiled, with TONs up to 100. Using dialkylborane derivatives and their corresponding bis(formyloxy)borates, HCOOH is decomposed to H₂ and CO₂, in the presence of a base, with high selectivity. Capitalizing on the mechanistic insights, current efforts are devoted to increase the catalytic activity of these new boron catalysts and explore the reduction chemistry of bis(formyloxy)borates.

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Notes and references
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† Electronic Supplementary Information (ESI) available: Experimental and computational procedures and physical properties of compounds. See DOI: 10.1039/b000000xs/

15. Contrary to trialkylboranes, 5 was found insensitive to acidic protonolysis during the catalysis and the cleavage of one of the Cₓ=ₓ-B bonds within the BBN backbone was never observed.
16. Although there is no experimental evidence for the formation of 9', isolation of the related [HC(O)OB(H)Ar'] union has been reported by Wang et al. see ref. 14.