Electrochemical Reduction of Carbon Dioxide to Methanol in the Presence of Benzannulated Dihydropyridine Additives

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\textbf{ABSTRACT:} Dihydropyridines (DHPs) have been postulated as active intermediates in the pyridine-mediated electrochemical conversion of CO\textsubscript{2} to methanol, however the ability of isolated DHPs to facilitate methanol production in a similar fashion to their parent aromatic N-heterocycles (ANHs) has not been tested. Here, we use bulk electrolysis to show that 1,2- and 1,4-DHPs (1,2-dihydrophenanthridine and 9,10-dihydroacridine) can mediate the sub-stoichiometric electrochemical reduction of CO\textsubscript{2} to methanol and formate with similar Faradaic efficiencies as the corresponding ANHs at Pt electrodes. 1,2-dihydrophenanthridine furthermore exhibits improved CO\textsubscript{2} reduction activity compared to its parent ANH (phenanthridine) at glassy carbon electrodes. These results provide the first experimental evidence for the participation of DHPs as additives in electrochemical CO\textsubscript{2} reduction.

\textbf{TOC GRAPHIC}
The recycling of CO₂ directly to liquid chemicals using water and a renewable energy source is a promising route to sustainable carbon-based fuels.\textsuperscript{1-2} Reports that the addition of simple aromatic N-heterocycles (ANHs) such as pyridine (1) leads to the production of methanol in acidic aqueous electrochemical\textsuperscript{3-6} and photochemical\textsuperscript{7-11} cells at low overpotentials or light-driven underpotentials have garnered both justifiable excitement\textsuperscript{12} and a healthy amount of scrutiny.\textsuperscript{13-14} Recent studies\textsuperscript{10,15-17} have verified that methanol is indeed produced and only in the presence of ANH additives, but also that multi-e\textsuperscript{-}/multi-H\textsuperscript{+} reduced products such as methanol and formic acid are generated with low, sub-stoichiometric turnover numbers (TONs; 0.04-0.33) with product selectivity and Faradaic efficiencies (%FE) dependent on the nature of the electrode used.\textsuperscript{3-4,7-8,15,18-19}

Given the promise of this simple system, the role of the ANH additive, the acidic solution and the electrode surface in the overall mechanism have been subject to ongoing debate. Computational studies from Carter, Musgrave, and furthered by Keith, suggest a critical role for 2e\textsuperscript{-}/2H\textsuperscript{+} reduced dihydropyridines (DHPs) as intermediates (Figure 1),\textsuperscript{20-23} either formed in solution\textsuperscript{22} or adsorbed to the electrode surface.\textsuperscript{20,24} A ‘weak-acid mechanism’\textsuperscript{13,25} has also been proposed where the conjugate acid of the ANH additive is reduced at the electrode surface to form adsorbed hydrogen, H\textsubscript{ads}, which then participates in proton-coupled hydride transfer (PCHT) with a second equivalent of [ANH-H]\textsuperscript{+} to facilitate CO₂ reduction\textsuperscript{26-27} but can also participate in hydrogen evolution.

Despite their prominence in computed mechanisms, the ability of isolated DHPs themselves to facilitate methanol production in a similar fashion to parent ANHs has to date not been tested. We hypothesized that if DHPs are competent intermediates, they should exhibit comparable activities to their parent ANHs. We therefore screened isolated
DHPs [1,2-dihydrophenanthridine (3-H₂) and 9,10-dihydroacridine (4-H₂)] as additives in electrochemical CO₂ reduction at both Pt and glassy carbon electrodes.

**Figure 1.** Structures of DHPs and related ANHs studied as additives in this work.

DHPs 3-H₂ and 4-H₂ are chemically similar to the 1,2- and 1,4-DHP isomers of 1-H₂ proposed as intermediates in pyridine-mediated CO₂ reduction (Figure 1). While a purely aqueous electrochemical system is more ideal for fuel-forming purposes, a mixed aqueous/organic solvent system was utilized here for solubility reasons. Accordingly, we also evaluated the activities of the parent ANHs phenanthridine (3; 3,4-benzoquinoline) and acridine (4; 2,3-benzoquinoline), as well as those of pyridine (1) and quinoline (2) in this mixed solvent system to enable comparisons with DHPs 3-H₂ and 4-H₂.

Bulk electrolyses were conducted to quantify yields of liquid fuel candidates methanol and formate. Potentiostatic electrolyses were used to ensure selectivity of the reductive processes, with \( E_{\text{applied}} \) and the charge passed chosen based on previously reported optimizations for 1 with a shift in the potential scale vs Fe⁰/⁺ due to the use of a mixture of solvents taken into account for accurate comparison of \( E_{\text{applied}} \). The \( E_{\text{applied}} = -0.75 \) V vs Fe⁰/⁺ used for experiments at Pt is at the onset of the reduction peak observed by CV for all the ANHs under CO₂ (Figure 3), while for reticulated vitreous carbon (RVC) electrodes \( E_{\text{applied}} = -1.20 \) V vs Fe⁰/⁺, at the onset of the reduction peaks observed in CVs.
for 1-3 at GCEs (Figure S9). Potentials were applied for ca. 10 000 s (see SI for CPE curves), with multiple analytical techniques (\textsuperscript{1}H NMR, GC-MS, GC-FID and LC-MS; see SI for experimental details and integration methods) employed to corroborate identification of specific organic products. Care was taken to address the potential for contamination during sample preparation and analysis (see SI).\textsuperscript{14}

From the GC and LC traces (see SI for chromatograms), the absolute yields of products obtainable under the conditions employed are low (10-250 \textmu{}M methanol and/or formate), consistent with absolute amounts observed in previous reports measuring the activity of 1 in aqueous electrochemical cells.\textsuperscript{3-4,7-8,15,17-18} As a result, the TONs we report for this system are sub-stoichiometric relative to the amount of DHP/ANH added (Table 1), in line with the literature on 1. The accuracy of the analytical techniques employed was checked using standard solutions, and the precision evaluated by running samples in triplicate and over a span of three months. The largest component of the error in our reported values based on GC-FID is attributed to sample-to-sample reproducibility in bulk electrolysis rather than the detection limit or consistency of the instruments used. \textsuperscript{1}H NMR (~3.24 ppm, see SI) and GC-MS corroborated the identification of methanol. The LC-MS method used for formic acid quantification proved less sensitive, and as such larger corresponding errors were determined for the reported values.

For DHPs 3-H\textsubscript{2} and 4-H\textsubscript{2}, %FEs determined from bulk electrolysis experiments at Pt are comparable with those observed for parent ANHs 3 and 4 (Table 1). Analysis of the electrolyzed reaction mixture by \textsuperscript{1}H NMR showed that ~40\% of 3-H\textsubscript{2} is converted to 3 after CO\textsubscript{2} reduction at Pt surfaces (Figure S19), with similar conversion of 4-H\textsubscript{2} to 4 under the same conditions. In comparison, potentiostatic electrolysis of 3-H\textsubscript{2} at the same
pH under Ar (in the absence of CO\textsubscript{2}) resulted in an order of magnitude lower conversion of \textit{3-H\textsubscript{2}} to \textit{3} (Figure S26), and 50\% less charge passed compared to under CO\textsubscript{2} (Figure 2a). This is consistent with the majority of the reactivity of the DHP and charge passed attributable to reaction of the DHP with CO\textsubscript{2}. The observed methanol and formic acid are therefore not simply products of an ANH-mediated process resulting from conversion of the DHP to its parent ANH under the conditions employed.

**Figure 2.** (a) Charge passed in bulk electrolyses of 10 mM \textit{3-H\textsubscript{2}} ($E_{\text{applied}}$ = -0.75 V vs Fe\textsuperscript{0/+}, Pt mesh electrode) under Ar (red dash) and two separate runs under CO\textsubscript{2} (black traces); comparison of CVs of 10 mM \textit{3-H\textsubscript{2}} (b) and \textit{4-H\textsubscript{2}} (c) under Ar at pH = 5.5 and under CO\textsubscript{2} (black) with CO\textsubscript{2} alone (blue), $v$ = 100 mV/s; 0.1 M LiClO\textsubscript{4} in CH\textsubscript{3}CN/H\textsubscript{2}O (40\% v/v), Pt disc; $E$ vs Fe\textsuperscript{0/+}.

Furthermore, electrolysis of \textit{3-H\textsubscript{2}} at RVC also led to methanol and formate production with similar %FE as seen at Pt electrodes, and with higher %FE than observed for \textit{3}. This demonstrates that isolated DHPs can function as additives in a similar fashion to their parent ANHs, which is consistent with the proposed role of DHPs as intermediates relevant in ANH-mediated reduction of CO\textsubscript{2} to methanol.\textsuperscript{21-24} No reduced products were detected when electrolysis of \textit{3-H\textsubscript{2}} under CO\textsubscript{2} was performed at a lower potential (-0.75 V vs. Fe\textsuperscript{0/+}) at RVC electrodes.
Table 1. Faradaic efficiencies for electrochemical CO$_2$ reduction in the presence of DHP or ANH additives

<table>
<thead>
<tr>
<th>Additive</th>
<th>Electrode</th>
<th>%FE$^a$ CH$_3$OH</th>
<th>%FE$^{b,c}$ HCOO$^{-}$</th>
<th>TON CH$_3$OH (10$^3$)</th>
<th>TOF CH$_3$OH (10$^3$ hr$^{-1}$)</th>
<th>TON HCOO$^{-}$ (10$^3$)</th>
<th>TOF HCOO$^{-}$ (10$^3$ hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt</td>
<td>30(10)</td>
<td>not det.</td>
<td>12.0(1.0)</td>
<td>4.3(4)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>RVC</td>
<td>7(7)</td>
<td>1.0(0.3)</td>
<td>0-4</td>
<td>0-1</td>
<td>0.76(24)</td>
<td>0.27(8)</td>
</tr>
<tr>
<td>2</td>
<td>Pt</td>
<td>36(16)</td>
<td>4(6)</td>
<td>15(7)</td>
<td>5.2(2.7)</td>
<td>6.6(9)</td>
<td>2.1(4)</td>
</tr>
<tr>
<td>2</td>
<td>RVC</td>
<td>11(7)</td>
<td>4(3)</td>
<td>3.9(1.9)</td>
<td>1.4(9)</td>
<td>0.8-20</td>
<td>0.2-5</td>
</tr>
<tr>
<td>3</td>
<td>Pt</td>
<td>12(8)</td>
<td>4(1)</td>
<td>7(3)</td>
<td>2.5(1.2)</td>
<td>5.4(1.0)</td>
<td>1.9(4)</td>
</tr>
<tr>
<td>3</td>
<td>RVC</td>
<td>5(3)</td>
<td>1.1(0.2)</td>
<td>2.2(1.6)</td>
<td>0.8(6)</td>
<td>1.56(22)</td>
<td>0.54(19)</td>
</tr>
<tr>
<td>3-H$_2$</td>
<td>Pt</td>
<td>19(7)</td>
<td>3(4)</td>
<td>9(3)</td>
<td>1.9(5)</td>
<td>0-8</td>
<td>0-2</td>
</tr>
<tr>
<td>3-H$_2$</td>
<td>RVC</td>
<td>15(7)</td>
<td>8(3)</td>
<td>4.3(2.4)</td>
<td>1.3(6)</td>
<td>5.9(2.2)</td>
<td>1.9(8)</td>
</tr>
<tr>
<td>4</td>
<td>Pt</td>
<td>17(13)</td>
<td>not det.</td>
<td>6(4)</td>
<td>2.1(1.6)</td>
<td>-</td>
<td>-</td>
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<tr>
<td>4</td>
<td>RVC</td>
<td>-$^d$</td>
<td>-$^d$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>4-H$_2$</td>
<td>Pt</td>
<td>13(10)</td>
<td>not det.</td>
<td>4(3)</td>
<td>1.2(9)</td>
<td>-</td>
<td>-</td>
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<tr>
<td>4-H$_2$</td>
<td>RVC</td>
<td>-$^d$</td>
<td>-$^d$</td>
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$^a$Via peak area of GC-FID traces (see SI) with standard deviation of bulk electrolysis samples. $^b$Via peak area from LC-MS traces (see SI). $^c$Signals for ANH overlap with product signals in $^1$H NMR. $^d$Significant electrode fouling (deposition).

Turning to the ANHs themselves, CO$_2$ reduction in the presence of an ANH additive was also seen at more inert electrode surfaces (RVC) at more reducing potentials.$^{31}$ 1-3 all exhibit a significant drop in %FE going from Pt to RVC electrodes with no products detected at a lower $E_{applied}$ (-0.75 V vs. Fe$^{0/+}$; RVC). The %FEs determined in this work for 1 are slightly higher, though not statistically different within error, than %FEs found reported for aqueous cells in the literature, though we note that in a mixed organic/aqueous solvent system CO$_2$ is expected to be more soluble,$^{32}$ and direct comparisons to literature %FEs should be made cautiously. Quinoline (2), recently proposed as a viable ANH additive on thermodynamic considerations,$^{33}$ exhibits the highest overall %FE and the highest methanol production of the series at both electrode surfaces. Pyridine (1) and acridine (4) exhibit the highest selectivity for methanol.
formation, with no formate observed by $^1$H NMR or LC-MS at Pt, indicating only trace amounts produced under our experimental conditions.

Unlike the correlation between $pK_a$ and total Faradaic yields previously reported for a series of substituted pyridines in water, the highest overall activity of 1-4 is observed for the ANH with an intermediate $pK_a$ (2). Lower %FEs are observed for ANHs with higher (1, 4) and lower (3) $pK_a$'s. The ease with which an ANH participates in a ‘weak acid’ reduction to form $H_{ads}$ is apparently not %FE determining in our system. This agrees with the observation that acetic acid, which has a $pK_a$ close to [1-H]$^+$, does not mediate methanol production.

To put into context the hydride donor ability of the DHPs, Musgrave estimated the hydride nucleophilicity ($N$) of 3-$H_2$ ($N_{3,H_2} \sim 8.1$) to be comparable to the experimentally determined value for the well-known hydride donor Hantzsch’s ester ($N = 9.00$). The experimentally determined value for 10-methyl-9,10-dihydroacridine, the $N$-methyl derivative of 4-$H_2$, is $N = 5.54$, while the 1,2-isomer of 1-$H_2$ is estimated to be the strongest DHP hydride donor ($N \sim 11.4$). The hydride nucleophilicity of ortho-1,2-dihydroquinoline (2-$H_2$) is reasoned to be intermediate between that of ortho-1,2-dihydropyridine (1-$H_2$) and 1,2-dihydrophenanthridine (3-$H_2$). This is on the basis that the remaining olefinic sub-unit in the partially hydrogenated ortho-2-$H_2$ retains conjugation with an intact aromatic benzo ring and is therefore stabilized with respect to the diene fragment of 1-$H_2$. In comparison, formation of 3-$H_2$ or 4-$H_2$ leaves in tact two aromatic benzo subunits. The reactivity of the isolated C=N bond towards hydrogenation in 3 is highlighted by the fact that the ‘imine-bridged, biphenyl’ resonance contributor dominates the ground state structure of 3, in accordance with Clar’s postulate. All have
been calculated to be competent hydride donors for CO\textsubscript{2} reduction based on thermodynamic considerations.\textsuperscript{22,33} \textbf{3-H\textsubscript{2}} has been used in the transfer hydrogenation of C=O bonds in \textalpha-ketoesters.\textsuperscript{36-37}

Combined with the calculated or experimental hydride nucleophilicities of the rest of the series, we estimate an order of decreasing hydride donor ability from \textbf{1-H\textsubscript{2}} > \textbf{2-H\textsubscript{2}} > \textbf{3-H\textsubscript{2}} > \textbf{4-H\textsubscript{2}}. We hypothesize that if the reactivity of ANH additives 1-4 is via formation of a DHP, the comparably high activity of 2 is derived from a balance between the Lewis acidity of the parent ANH (ease of formation of a DHP, lower susceptibility to side reactions) and hydride donor ability of the DHP once formed. Keith has similarly proposed on the basis of quantum chemistry thermodynamic calculations that ANH-mediated multi-e\textsuperscript{-}/multi-H\textsuperscript{+} CO\textsubscript{2} may be governed by the Sabatier Principle, where Brønsted acidity and hydride donor ability must be balanced to manage both H\textsuperscript{+} and H\textsuperscript{-} transfer to CO\textsubscript{2}.\textsuperscript{33} While phenanthridine (3) and acridine (4) mediate reduction of CO\textsubscript{2} with similar %FEs, 4 additionally undergoes a more prominent deposition process (see Figure S6). Access to \textit{ortho}- (available in 3, not available in 4) or \textit{para}-positions (available in 4, not available in 3) likely governs the interaction of an ANH at the electrode surface. Electrochemical deposition of 1,10-phenanthroline in acid, for example, was shown to occur via covalent modification of GCE surfaces through the \textit{para}-position of the ANH.\textsuperscript{38-39}

The differences in %FE observed at Pt compared with RVC for the ANH series and the lower applied potential is consistent with an important role for the electrode surface in the observation of CO\textsubscript{2} reduction.\textsuperscript{20-21,24,40} Nevertheless, we tested the possibility of a homogeneous reaction between CO\textsubscript{2} and DHPs \textbf{3-H\textsubscript{2}} and \textbf{4-H\textsubscript{2}} by conducting NMR scale
reactions of $3\text{-H}_2/4\text{-H}_2$ under CO$_2$ (1 atm) in CD$_3$CN/D$_2$O (1:0.1 v:v) to probe the chemical reactivity in the absence of an electrode surface or applied potential. $^1$H NMR analysis showed no observable conversion of DHP to ANH at room temperature, and no CO$_2$-derived products, H$_2$ generation, or H/D scrambling (Figures S23-S24), in agreement with reported results for $1/1\text{-H}_2$ mixtures and 1 with Pt nanoparticles.$^{9,25}$ The absence of direct chemical reaction suggests that participation of the electrode surface and an applied potential is critical for CO$_2$ reduction mediated by a pre-formed DHP in an electrochemical system.$^{24,41-42}$

CVs of DHPs $3\text{-H}_2/4\text{-H}_2$ in the absence of CO$_2$ showed no reductive events in initial cathodic scans of neutral or acidic solutions at Pt (Figure 2b) or GCE (Figure S11). Cathodic current can be observed after cycling through a $2e^-/2H^+$ electrochemical oxidation (0.3-0.5 V vs Fe$^{0/+}$), with this new reductive event accordingly assigned to reduction of newly formed $[3\text{-H}]^+/[4\text{-H}]^+$ (Figure S11).$^{43}$ Introduction of CO$_2$ results in the appearance of an irreversible reduction at -0.8 V vs Fe$^{0/+}$ when the potential is initially swept from the open circuit potential for $3\text{-H}_2$, with a large current enhancement compared to the initial cathodic scan under acidic conditions (Ar) and for a CO$_2$ saturated solution without any $3\text{-H}_2$ present (Figure 2b). At the potentials applied in the bulk electrolysis reactions, DHPs $3\text{-H}_2/4\text{-H}_2$ therefore only exhibit an appreciable current response by CV at the scan rates examined in the presence of CO$_2$. In other words, for pre-formed DHPs, all four components – $3\text{-H}_2$, CO$_2$, an electrode and a sufficiently reducing potential – are required to observe methanol production in bulk electrolysis, and current enhancement by CV.
In comparison, CVs of ANHs 1-4 at Pt in the absence of CO\textsubscript{2} but under similar acidic conditions show a quasi-reversible reduction at \(-0.7\) V vs Fe\textsuperscript{0+/+}, with a scan rate dependence corresponding to diffusion control (see SI). A linear correlation is observed between \(E_{1/2}\) and ANH pK\textsubscript{a}, with a slope of -0.054 mV/[unit pH], indicating the ‘weak acid’ relationship observed in water\textsuperscript{13,25} is preserved in mixed CH\textsubscript{3}CN/H\textsubscript{2}O (see Figure S1, Equation 1 in SI).

Introduction of CO\textsubscript{2} to the ANH solution results in an increase in the current observed on the CV timescale for 1-3 (Figure 3), though only for 1 and 2 is the enhancement above the sum of the background currents (\(J_{\text{ANH-ANH-H}^+} + J_{\text{CO2}}\)) at the scan rates employed. In aqueous solution, increased cathodic current for solutions of 1 in the presence of CO\textsubscript{2} was only detected at scan rates less than 10 mVs\textsuperscript{-1}.\textsuperscript{44} For 3, the enhancement is not significant compared to the sum of the background currents (\(J_{3/3-H}^+ + J_{\text{CO2}}\); Figure 3c).\textsuperscript{13,19} At the scan rates employed (100 mV/s), this current enhancement is likely a result of the presence of dissolved CO\textsubscript{2}/H\textsubscript{2}CO\textsubscript{3} in solution as described previously.\textsuperscript{13,44} In a recent study, Rybchenko et al. confirmed that, in addition to methanol production, hydrogen evolution is the dominant electrochemical reaction in 1-containing aqueous electrolyte solution at Pt, even under high CO\textsubscript{2} pressure. Methanol production with \%FE of up to 10% for the first 5-10 C cm\textsuperscript{-2} can be reproducibly detected but only after \(ca.\) 1 hr of electrolysis.\textsuperscript{17} As a result, only a small to negligible current enhancement is expected on the CV timescale (ms to s) for CO\textsubscript{2} reduction in the presence of ANH additives chemically similar to 1.

The reduction processes for 1-4 under CO\textsubscript{2} are quasi-reversible, and show features of diffusion control (see Randles-Sevcik plots in SI, Figure S5) with no peak current
saturation observed, indicating that it is unlikely we are observing an electrocatalytic process on the CV timescale (Figure S4). In comparison, the current enhancement for $3$-$H_2$ under CO$_2$ is five-fold larger in magnitude with a 25% increase in the total current passed under CO$_2$ compared to its parent ANH $3$. No current enhancement above the background currents was observed for $4$-$H_2$ under CO$_2$, similar to $4$.

Figure 3. CVs 1 atm CO$_2$ (black); under Ar in acid (red); and CO$_2$ alone (1 atm, blue) for 10 mM of (a) $1$, pH = 5.5; (b) $2$, pH = 5.3; (c) $3$, pH = 5.2; (d) $4$, pH = 5.7. $v$ = 100 mV/s; 0.1 M LiClO$_4$, CH$_3$CN/H$_2$O (40% v/v), Pt disc; $E$ vs Fc$^{0/+}$.

Given the electrode dependence of the %FEs for CO$_2$ reduction by ANHs and the absence of product formation by DHPs both without any applied potential or at RVC electrodes at lower $E_{applied}$ (-0.75 V), a strictly solution-based DHP mechanism for CO$_2$ reduction appears unlikely.$^{22,45}$ Lessio et al. recently established that a surface-bound 2-pyridinyl radical formed via transfer of photoexcited electrons from p-GaP to $[1$-$H]^+$ is thermodynamically feasible in silico, and calculated to be more reactive than the more stable surface-adsorbed DHP $[1$-$H_2]_{ads}$ (Figure 4a).$^{24}$ Both are proposed as competent intermediates in ANH-mediated photoelectrochemical CO$_2$ reduction at p-GaP.
In our system, reactivity via surface-adsorbed $[3\text{-H}_2]_{\text{ads}}$ directly does not account for the appearance of a reductive event in CVs of $3\text{-H}_2$ under CO$_2$ (Figure 2b). Formation of a surface-bound DHP-derived radical ($\text{DHP}^*_{\text{ads}}$; Figure 4b) via H$_{\text{ads}}$ would explain the observation that different potentials are required for methanol and formate production in bulk electrolyses of DHPs $3\text{-H}_2$ and $4\text{-H}_2$ at RVC compared with Pt, as the surfaces require different potentials for H$_{\text{ads}}$ formation, and that no homogenous reactivity occurs between $3\text{-H}_2$/4-H$_2$ and CO$_2$ in the absence of an electrode/potential.

**Figure 4.** (a) Mechanism for ANH-based CO$_2$ reduction via DHP$_{\text{ads}}$ or DHP$^*_{\text{ads}}$ (adapted from reference [24])

(b) DHP-based CO$_2$ Reduction (this work)
The mechanism proposed in Figure 4 would account for all the components required to observe methanol production: \( \text{3-H}_2 \), \( \text{CO}_2 \), a surface and a sufficiently reducing potential. Participation of \( \text{H}_{\text{ads}} \) (formed via ‘weak-acid reduction’ of carbonic acid in solution, as observed in the background current of \( \text{CO}_2 \) alone, Figure 2b)\(^{44} \) accounts for the difference in potential required for methanol production at RVC vs Pt. \( \text{CO}_2 \) reduction is postulated to then occur via hydride transfer from the DHP-derived surface species, potentially stabilized by surface-organized waters,\(^{22} \) followed by proton transfer from the acidic solution completing the initial reduction to formic acid. Bulk electrolyses of ANHs under \( \text{CO}_2 \) in dry, acidified \( \text{CH}_3\text{CN} \) at RVC and Pt electrodes resulted in no observable \( \text{CO}_2 \) reduction products, indicating a critical role for water in the reduction mechanism.

The formation of \( \text{H}_{\text{ads}} \) also appears to be critical to the activity of ANH additives and we cannot distinguish here a PCHT mechanism\(^{27} \) or reactivity of a surface-bound DHP\(_{\text{ads}} \) or DHP-derived radical generated via \( \text{H}_{\text{ads}} \), as proposed by Carter.\(^{24} \) The decrease in %FE of the ANHs moving from Pt to RVC could result from increased ANH adsorption on RVC surfaces, though only 4 was observed to form a noticeable film after electrolysis under \( \text{CO}_2 \) at Pt surfaces and after one CV cycle at GCEs (Figure S6). A poisoning effect at high concentrations of 1 on CuInS\(_2 \) has been attributed to formation of an pyridine adsorption layer that leads to increased resistance to mass transfer.\(^{16} \)

In conclusion, we present here the first evidence for the participation of isolated dihydropyridine-type species in surface-dependent electrochemical \( \text{CO}_2 \) reduction. This is based on the following observations: (1) methanol and formic acid are generated in electrolyses of isolated DHPs \( \text{3-H}_2 \) or \( \text{4-H}_2 \) under 1 atm of \( \text{CO}_2 \) at both Pt and RVC electrodes; (2) CV and NMR studies show that the parent ANHs 3 and 4 are not
generated from the corresponding DHPs in appreciable amounts in the absence of CO₂, ruling out ANH-only mediated activity; (3) no homogeneous reactivity is observed between DHPs 3-H₂ or 4-H₂ and CO₂ in the absence of an electrode surface/applied potential; and (4) DHP 3-H₂ exhibits an electrode dependence (Pt vs RVC) on the \( E_{\text{applied}} \) required to observe methanol production, though not on the observed %FE.

The ability to carry out electrochemical CO₂ to methanol conversion using carbon-based electrodes instead of precious metals such as Pt or Pd is an important milestone for the scaleability of reduction schemes employing DHP or ANH additives.\(^{46-48}\) Consistent with previous studies on 1, however, the overall yields of reduced organic products in our experiments remain sub-stoichiometric, even in reactions mediated by pre-formed DHPs. Moreover, we did not observe evidence of electrochemical generation of DHP 3-H₂ from ANH 3. These experimental findings will hopefully motivate better understanding of the mechanism of multi-H⁺/e⁻ processes occurring in CO₂ electrochemical reduction in the presence of simple organic additives, and lead to the improvements in turnover numbers, for example, by targeting biomimetic hydride shuttles capable of cooperative interactions with electrode surfaces and electric potentials.\(^{24,49-51}\)

ASSOCIATED CONTENT

Supporting Information. Full experimental details, supporting figures and tables; NMR spectra, GC and LC traces from bulk electrolysis samples (PDF). The Supporting Information is available free of charge on the ACS Publications website.

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Funding Sources

The Natural Sciences Engineering Research Council of Canada is gratefully acknowledged for a Discovery Grant to DEH (RGPIN-2014-03733) and a CGS-M Fellowship (PKG), as is the University of Manitoba for start-up funding (DEH) and GETS (PKG) support.

ACKNOWLEDGMENT

We thank Prof. Gregg Tomy for access to a LC-MS; MCAL (Dr. Tom Ward) for access to a GC-MS and GC-FID; Dr. Kirk Marat for assistance with NMR solvent suppression; and Thor Halldorson for helping develop a LC-MS method.

REFERENCES


(28) Minimal CH₃CN was required to dissolve 3/4 in water, and so for consistency the same solvent ratio was used all compounds. LiClO₄ chosen as the electrolyte due to its ability to dissolve in aqueous/non-aqueous mixtures.
In our experimental set-up, %FE for hydrogen (H₂) was not determined as CO₂ is bubbled through the solution continuously.


pKa’s in CH₃CN/H₂O were experimentally determined. See SI.


(43) Oxidative cycling was only conducted in survey CV scans, and was not performed prior to bulk electrolysis experiments of the DHP samples.


