The Selective Electrochemical Conversion of Preactivated CO2 to Methane

Oana R. Luca,* Charles C. L. McCrory,* Nathan F. Dalleska, and Carl A. Koval* a, b

a Joint Center for Artificial Photosynthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA
b Environmental Analysis Center, California Institute of Technology, Pasadena, California 91125, USA

Results and Discussion

CO2 reduction poses significant challenges in terms of chemical reactivity. Although progress has been made in the realm of heterogeneous catalysis for the electroreduction of CO2, the selective reduction of CO2 to highly-reduced (>6 e−) products with high faradaic efficiency remains an obstacle in the technological implementation of a solar fuel device.15

In order to overcome the kinetic limitations and the consequent high overpotentials typically observed for electrochemical reduction of CO2, we explored the possibility of converting CO2 into a different species, thus potentially circumventing the challenges generally encountered in the direct reduction of CO2.

N-heterocyclic carbenes (NHCs) are strong Brønsted bases with conjugate acids with pKₐ values that vary between 17 and 25, comparable to alkoxides.24 They are capable of reacting with ketenes forming [1,2]-dipolar species that can undergo subsequent reactions with electrophiles and nucleophiles (Figure 1a).25 In a directly analogous reaction, N-heterocyclic carbenes can reversibly react with CO2 (Figure 1b), although their subsequent reactions with electrophiles and nucleophiles have not been explicitly explored. NHCs have previously been reported to be competent organocatalysts for the hydrolysis of CO2 to a 6e− reduced product: methanol.16–18

N-heterocyclic carbenes (NHCs) are known to reversibly react with CO2 to form zwiterionic imidazolium carboxylates.25 We now exploit the chemical opportunity to develop a preactivation of our desired substrate (Figure 1b). A free NHC allows us to capture, bend, and thus transform CO2 to a different chemical entity prior to any chemical transformation. Known modes of CO2 activation with molecular species often involve binding to low-valent nucleophilic metal centers.23 Organic activators such as frustrated Lewis Acid/Base pairs have also been reported.22 Our strategy involves the capture of CO2 with a free NHC to form a zwiterionic NHC-CO2 carboxylate, which is distinct from the Lewis Acid/Base methodology.

Figure 2 shows cyclic voltammograms of [Ni(cyclam)]⁺⁺ and the proton source trifluoroethanol in CH₂Cl₂ under various conditions. In the absence of CO2 (black curve), very little reduction current was observed at electrode potentials positive of ca. −2.0 V. Addition of CO2 to the electrolyte solution resulted in enhanced cathodic current at potentials negative of ca. −1.3 V (blue curve), consistent with previous reports of the electrochemistry of the Ni(cyclam)⁺⁺ cation in nonaqueous solvents in the presence of CO2.23 In contrast, addition of

*Electrochemical Society Active Member.
†E-mail: koval@colorado.edu

© The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC-BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. DOI: 10.1149/2.0371507jes All rights reserved.

Figure 1. (a) Reversible binding of ketenes as CO2 analogues can be achieved with by a N-heterocyclic carbene24 (b) Reversible binding and bending of CO2 with by a N-heterocyclic carbene24 (c) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (d) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (e) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (f) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (g) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (h) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (i) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (j) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (k) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (l) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (m) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (n) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (o) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (p) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (q) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (r) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (s) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (t) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (u) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (v) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (w) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (x) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (y) Reversible binding and bending of CO2 with N-heterocyclic carbene24 (z) Reversible binding and bending of CO2 with N-heterocyclic carbene24
NHCO₂⁻ with unreacted CO₂ either absent or present (magenta and green curves, respectively), results in CVs with enhanced cathodic currents of ~ –1.5 to 1.7 V vs (Ag/AgNO₃). The enhanced currents at more positive electrode potentials observed when the NHCO₂⁻ was present suggested a CO₂ reduction pathway different from what is observed with unreacted CO₂, and this hypothesis was subsequently confirmed with a series of controlled potential electrolysis (CPE) experiments. Additional background cyclic voltammograms are shown in Figure M1 (in the Supporting Info).

While it is tempting to compare the (over)potentials observed for the reduction of NHCO₂⁻ with thermodynamic values for CO₂ reduction in aqueous electrolytes, or with studies conducted in other nonaqueous electrolytes, quantitative comparisons are problematic for a variety of reasons. Even in aqueous electrolytes, comparison of the reduction potentials from the literature for CO₂ reduction is complicated by inadequately defined and/or controlled electrolyte pH, reaction products not being present during the measurements, and reporting of overpotential values without an associated current density. Even greater difficulties exist for comparisons involving CO₂ reduction in nonaqueous electrolytes, including different nonaqueous reference electrode conventions and their relationship to the NHE or RHE, and the fact that the activities of protons and water vary widely for different non-aqueous solvents, making it difficult to define thermodynamically relevant quantities. Nevertheless, it is certain that the reduction of CO₂ to methane reported here would require substantial overpotential if it proceeded catalytically via the electrochemical formation of the NHCO₂⁻ adduct from NH⁻H⁺, which along with methane is a product of the electrolysis.

A series of preparative-scale CPE experiments combined with analyses of the cell headspace by GC-TCD and GC-MS was used to confirm the identity and source of electrolysis products. Each electrolysis experiment was conducted for two hours at ~ –1.5 V (vs Ag/AgNO₃) and the results are summarized in Table I. As expected from the CVs, electrolysis of solutions that did not contain [Ni(cyclam)]²⁺ and carboxylate, resulted in relatively little current passed and generated only small amounts of CO and H₂ as products. In contrast, when [Ni(cyclam)]²⁺ and carboxylate were present in the electrolyte, the electrolysis charge was significantly greater and the sole electrolysis product observed in GC-TCD analysis of the headspace was methane (Figure M2). Quantitation of the methane peak and comparison with the electrolysis charge allowed calculation of a faradaic efficiency > 93% for the 8e⁻ reduction of the NHCO₂⁻ to methane. After electrolysis, the surface of the working electrode was analyzed with X-ray photoelectron spectroscopy (XPS) to test for the presence of any adsorbed Ni or other transition metal materials (Figure M5 and M6). No Ni or other transition metal materials were detected within the ~0.1 atom% detection limit of XPS.

Somewhat surprisingly, in the absence of [Ni(cyclam)]²⁺ in the electrolysis solution, we observed the formation of a 12/1 H₂/CH₄ mixture with satisfactory faradaic efficiency, suggesting that glassy carbon is also capable of reducing NHCO₂⁻ to CH₄ product, although with poor selectivity. There is always a possibility that small amounts of Ag⁺ from the reference electrode may contribute to the production of CH₄ in the absence of [Ni(cyclam)]²⁺, although we see no evidence of Ag contamination on our working electrode post-electrolysis within the ~ 0.1 atom % detection limit of XPS. Also, from the control experiment in the absence of [Ni(cyclam)]²⁺, it can be concluded that any possible contribution of trace Ag to the production of CH₄ is small, and therefore does not contribute appreciably to the observed catalysis in the presence of [Ni(cyclam)]²⁺.

The source of the carbon contained in the methane found in the headspace after CPE was determined by isotopic labeling of various reactants and GC-MS analysis of the products. By performing CPE in deuterated methylene chloride (CD₂Cl₂), unlabeled trifluoroethanol and CO₂-NH⁻, labeled CH₄ is the exclusive product observed indicating that the source of carbon in the electrochemically produced methane is the CO₂ bound to the NHC fragment (Figure 3 for the GC-TOF EI trace for the ¹³CH₄ exact mass detection). In Figure 3 the molecular ion ¹³CH₄⁺ is clearly resolved from OH⁺, and is at the expected exact mass 17.01356 + 0.00011.

Table 1. Control potential electrolyses for the reduction of pre-activated CO₂⁻.

<table>
<thead>
<tr>
<th>Components</th>
<th>Charge passed</th>
<th>Product</th>
<th>Faradaic efficiency</th>
<th>Moles of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(cyclam)]²⁺, CF₃CH₂OH, NHCO₂⁻, CO₂</td>
<td>29 ±6 C</td>
<td>CH₄</td>
<td>91±4%</td>
<td>3.3×10⁻⁵</td>
</tr>
<tr>
<td>[Ni(cyclam)]²⁺, CF₃CH₂OH, NHCO₂⁻, N₂</td>
<td>27 ±5 C</td>
<td>CH₄</td>
<td>93±2%</td>
<td>3.2×10⁻⁵</td>
</tr>
<tr>
<td>CF₃CH₂OH, NHCO₂⁻, N₂</td>
<td>8 ±5 C</td>
<td>H₂:CH₄ (12:1)</td>
<td>80±7%</td>
<td>3.1×10⁻⁵ 5.2×10⁻⁶</td>
</tr>
<tr>
<td>[Ni(cyclam)]²⁺, NHCO₂⁻, N₂</td>
<td>10 ±7 C</td>
<td>CO</td>
<td>78±10%</td>
<td>4.0×10⁻⁵</td>
</tr>
<tr>
<td>[Ni(cyclam)]²⁺, CF₃CH₂OH, CO₂, N₂</td>
<td>9 ±7 C</td>
<td>H₂, CO (1:2)</td>
<td>72±12%</td>
<td>1×10⁻⁵ : 2.2×10⁻⁵</td>
</tr>
<tr>
<td>[Ni(cyclam)]²⁺, CF₃CH₂OH, N₂</td>
<td>5 ± 2 C</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

a. 0.2 M Bu₄NBF₄ solution in 60 ml of a 4:2 (v:v) methylene chloride/trifluoroethanol mixture. The working chamber volume was 40 ml and the counter chamber volume was 20 ml within a total cell volume of 188.5 ml. The experiment was run with a CO₂-saturated solution with an added 466 mg of the 1,3-bis(2,6-diisopropylphenyl)imidazolium carboxylate 1 (MW: 452.5 g/mol) and 3.4 mg [Ni(cyclam)]Cl₂ (MW: 320 g/mol).
b. 10 ml of the headspace volume were sampled after 2h of electrolysis at ~ –1.5 V and analyzed by an Agilent GC-TCD instrument.
c. Faradaic efficiencies were calculated assuming an 8e⁻ transformation per mol of CH₄ detected, a 2e⁻ transformation per mol of H₂ detected, and a 2e⁻ transformation per mol of CO detected.
Figure 3. 13C Labeling experiments for the reduction of NHC-CO2- 13C. (a) Chemical equation for the 13C-labeling experiment in the selective electrochemical conversion of CO2 to methane. (b) Water-resolved mass spectrum of an electrolysis headspace sample for the 13C-labeling experiment.

mass. 13CH4+ appears at an intensity consistent with electron impact library mass spectra of methane, and at the expected mass(16.029 m/z measured, 16.027 m/z calculated). Our mass calibration is confirmed by the measured mass of O(15.997 m/z measured, 15.995 m/z calculated). CH4+ is 16.031 m/z calculated) and would be expected to appear at 16.033 m/z with the present calibration. There is no evidence of a shoulder on the 13CH4+ peak or of a separate peak at the position expected for unlabeled methane. We did not detect any evidence of D-incorporation in the methane detected in the headspace, thus suggesting that solvent participation is not occurring in the chemistry under our conditions. In a similar experiment, we performed the electrochemical transformation in the presence of deuterated trifluoroethanol and unlabeled methylene chloride with NHC-13CO2 (Figure M8). We observed a response of mass peak 21 m/z with the appropriate isotopic distribution (21/19/17 m/z) corresponding to the formation of 13CH4+ (Figures M8 and M9 in the SI).

In order to determine the fate of the organic fragments left behind in this transformation, we performed a standard organic workup and analyzed the sample by UPLC-MS. The data revealed that the major organic species left in solution, after workup is protonated 1,3-bis(2,6-diisopropylphenyl)imidazolium with 389 m/z (Figures M3 and M4 in the SI).

We were able to identify two other organic fragments in the liquid phase analysis (M4), possibly indicating the participation of C-bound intermediates in the observed chemistry.

In conclusion, we report the electrode-driven conversion of imidazolium carboxylates, acting as CO2 surrogates, directly to methane. The product of this transformation is an 8 e- , high-value product that was achieved by implementing an unprecedented preactivation motif. We used [Ni(cyclam)Cl2], a known electrocatalyst for CO2 reduction to CO as mediator for the transformation. Further studies are under way to elucidate the mechanism of the transformation.

Methods

All reagents were received from commercial sources and used without further purification unless otherwise specified. Solvents were dried by passage through a column of activated alumina followed by storage under dinitrogen. Ni(cyclam)Cl2 and NHC-CO2 were prepared as previously described.23,25

GC measurements were collected using an Agilent Technologies 7890A GC system with front and back TCD channels. GC-MS-TOF and exact mass analyses were performed on a GC-MS using an Agilent 6890 gas chromatograph interfaced to a Waters GCT Premier time-of-flight. All electrochemical experiments were performed using either a Bio-Logic VSP-300 multichannel potentiotstat/galvanostat or a BioLogic VSP-400 potentiostat/galvanostat. All electrochemical data was recorded using the Bio-Logic EC Lab Express (5.53) software package.

The reference electrode for all electrochemical measurements was a Ag/AgNO3 (0.5 mM)/CH2Cl2 nonaqueous reference electrode (also contained 0.1 M Bu4NBuF4) separated from the solution by a Vycor (Bioanalytical Systems, Inc.) and externally referenced to ferrocene. We report the potentials vs Ag/AgNO3, but we also provide an alternate Fe/Fe+ scale for reference in each of the cyclic voltammogram figures.

The surface speciation of the carbon electrode was determined via XPS on a Kratos Axis Nova spectrometer with DLD (Kratos Analytical; Manchester, UK). The excitation source for all analysis was monochromatic Al Kα1,2 (hv = 1486.6 eV) operating at 30 mA and 15 kV.28,29

Additional details are available in the Supporting Information.

Acknowledgments

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U. S. Department of Energy under Award Number DE-SC0004993. The authors thank Professors Jonas Peters, T. Don Tilley, Clifford Kubiak and Nathan Lewis for many insightful discussions. We thank Dr. Slobodan Mitrovic and Natalie Becerra for help with the XPS analyses, Ryan Jones and Katherine Schilling for technical support and Rick Gerhardt for help with the electrochemical cell design. ORL and CCLM performed electrochemical experiments. CCLM analyzed the XPS data, NFD aided in the labeling experiments. CAK advised the research. ORL had the idea for the project. ORL, CCLM, NFD and CAK wrote the manuscript.

References