



The Selective Electrochemical Conversion of Preactivated CO₂ to Methane

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

^aJoint Center for Artificial Photosynthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

^bEnvironmental Analysis Center, California Institute of Technology, Pasadena, California 91125, USA

This work reports the selective electrochemical conversion of CO₂ to methane, the reverse reaction of fossil fuel combustion. This reaction is facilitated by preactivation of the CO₂ molecule with an N-heterocyclic carbene (NHC) to form a zwitterionic species in the first step. In the presence of Ni(cyclam)²⁺ and CF₃CH₂OH, this species is shown to undergo further electrochemical reduction of the bound-CO₂ fragment at glassy carbon cathodes in dichloromethane electrolyte solution. Labeling studies confirm the origin of the carbon and protons in the methane product are the preactivated CO₂ and trifluoroethanol respectively.

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As renewable, intermittent power sources such as solar and wind become an increasingly important part of the global energy portfolio, there is a concurrent need for efficient energy storage.¹⁻³ Although many storage strategies exist, one of the most promising is the electrochemical production of carbon-containing chemical fuels from carbon dioxide (CO₂) using earth-abundant catalysts.⁴⁻⁹ However, selective electrochemical conversion of CO₂ by greater than 2 e⁻ to products such as methanol (CH₃OH, 6 e⁻)¹⁰⁻¹¹ and methane (CH₄, 8 e⁻) has not yet been achieved.¹²⁻¹⁵ We now report the first selective conversion of CO₂ to an 8 e⁻ reduced product by preactivating CO₂ with organic compounds to form CO₂-adducts with lower activation barriers to subsequent reduction steps.^{11,16-22} We used N-heterocyclic carbenes (NHCs), specifically 1,3-bis(2,6-diisopropylphenyl)imidazole, that are known to readily react with CO₂ to form neutral zwitterionic NHC-CO₂ adducts, also reported as intermediates in organocatalytic reduction chemistry.¹⁶⁻²²

Herein we report the direct electrochemical conversion of CO₂ to CH₄ via the reduction of 1,3-bis(2,6-diisopropylphenyl)imidazolium carboxylate, NHC-CO₂, at a carbon electrode in the presence of a [Ni(cyclam)]²⁺ mediator²³ with CF₃CH₂OH as a proton source. The sole observed gas product of this electrochemical conversion is CH₄ with >93% faradaic efficiency. ¹³C-labeling experiments show that after ¹³CO₂ is first converted to NHC-¹³CO₂, it is then reduced to ¹³CH₄. Further deuterium-labeling experiments show the proton source in the observed ¹³CD₄ is CF₃CH₂OD. CH₄ as the selective reduction product formed from CO₂, has the advantage of maximal CH bonds and thus maximal calorific content. As a relatively inert gaseous product, it overcomes separation issues that a liquid CO₂ reduction product would bring in a solar fuel device. Our results demonstrate the viability of a preactivation strategy toward the selective, electrochemical conversion of CO₂ by 8e⁻.

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 obstacle¹⁴ 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 pK_a 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).²⁴ 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 hydrosilylation of CO₂ to a 6e⁻ reduced product: methanol.¹⁶⁻¹⁸

N-heterocyclic carbenes (NHCs) are known to reversibly react with CO₂ to form zwitterionic 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 zwitterionic NHC-CO₂ carboxylate, which is distinct from the Lewis Acid/Base methodology.

Figure 2 shows cyclic voltammograms of [Ni(cyclam)]²⁺ 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)²⁺ cation in nonaqueous solvents in the presence of CO₂.²³ In contrast, addition of

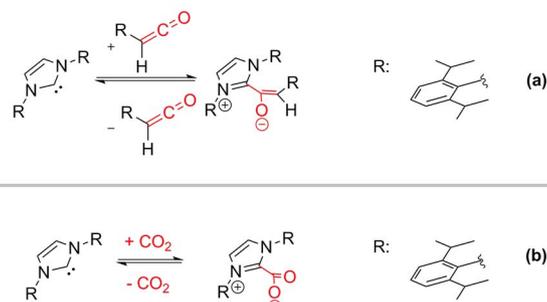


Figure 1. (a) Reversible binding of ketenes as CO₂ analogues can be achieved with a N-heterocyclic carbene²⁴ (b) Reversible binding and bending of CO₂ by an NHC as preactivation motif in the reduction of CO₂ in the current work.

*Electrochemical Society Active Member.

^zE-mail: koval@colorado.edu

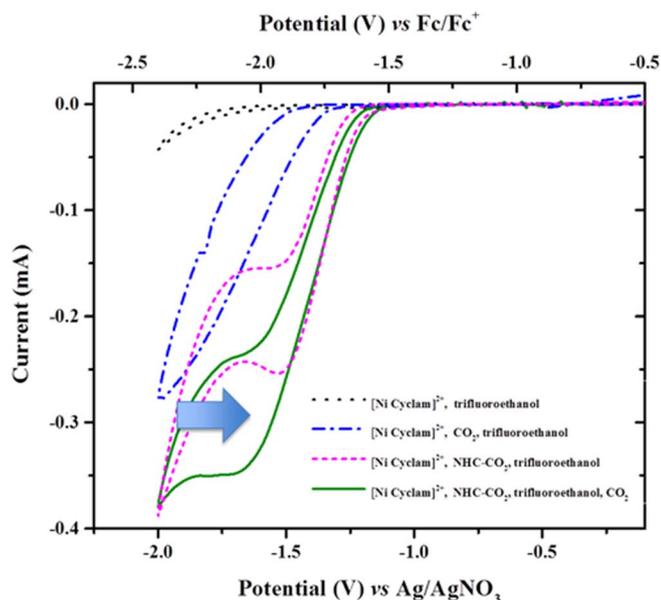


Figure 2. Cyclic voltammograms for reduction of 1,3-bis (2,6-diisopropylphenyl)imidazolium carboxylate, NHC-CO₂, to methane with the preactivated CO₂ carboxylate molecule. Note the shift of the reduction potential from the catalytic run for CO₂ reduction versus the high-current irreversible electrochemical response in the presence of NHC-CO₂, as CO₂ surrogate. Conditions: 5 ml CH₂Cl₂ 0.1 M *n*Bu₄NBF₄, 0.5 ml trifluoroethanol, 1.2 mM [Ni(cyclam)]Cl₂, 24 mM NHC-CO₂, scan rate = 100 mV/s.

NHC-CO₂ with unreacted CO₂ either absent or present (magenta and green curves, respectively), results in CVs with enhanced cathodic currents negative of -1.1 V and distinct waves with peak potentials ranging from -1.5 to 1.7 V vs (Ag/AgNO₃). The enhanced currents at more positive electrode potentials observed when the NHC-CO₂ 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 NHC-CO₂ 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 overpotentials reported in 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 den-

sity. 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 NHC-CO₂ adduct from NHC-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 carried out 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 process 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 NHC-CO₂ 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.^{26,27}

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 NHC-CO₂ 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 ¹³CO₂-NHC, ¹³CH₄ 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

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

Components ^a	Charge passed	Product ^b	Faradaic efficiency ^{c,d}	Moles of product
[Ni(cyclam)] ²⁺ , CF ₃ CH ₂ OH, NHC-CO ₂ , CO ₂	29 ± 6 C	CH ₄	91 ± 4%	3.3 × 10 ⁻⁵
[Ni(cyclam)] ²⁺ , CF ₃ CH ₂ OH, NHC-CO ₂ , N ₂	27 ± 5 C	CH ₄	93 ± 2%	3.2 × 10 ⁻⁵
CF ₃ CH ₂ OH, NHC-CO ₂ , N ₂	8 ± 5 C	H ₂ :CH ₄ (12:1)	80 ± 7%	3.1 × 10 ⁻⁵ ; 2.5 × 10 ⁻⁶
[Ni(cyclam)] ²⁺ , NHC-CO ₂ , N ₂	10 ± 7 C	CO	78 ± 10%	4.0 × 10 ⁻⁵
[Ni(cyclam)] ²⁺ , CF ₃ CH ₂ OH, CO ₂ , N ₂	9 ± 7 C	H ₂ , CO (1:2)	72 ± 12%	1 × 10 ⁻⁵ ; 2.2 × 10 ⁻⁵
[Ni(cyclam)] ²⁺ , CF ₃ CH ₂ OH, N ₂	5 ± 2 C	n/a	n/a	n/a

^a0.2 M *n*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: 432.5 g/mol) and 3.4 mg [Ni(cyclam)]Cl₂ (MW: 320 g/mol).

^{b,c}10 ml of the headspace volume were sampled after 2h of electrolysis at -1.5 V and analyzed by an Agilent GC-TCD instrument.

^dFaradaic 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.

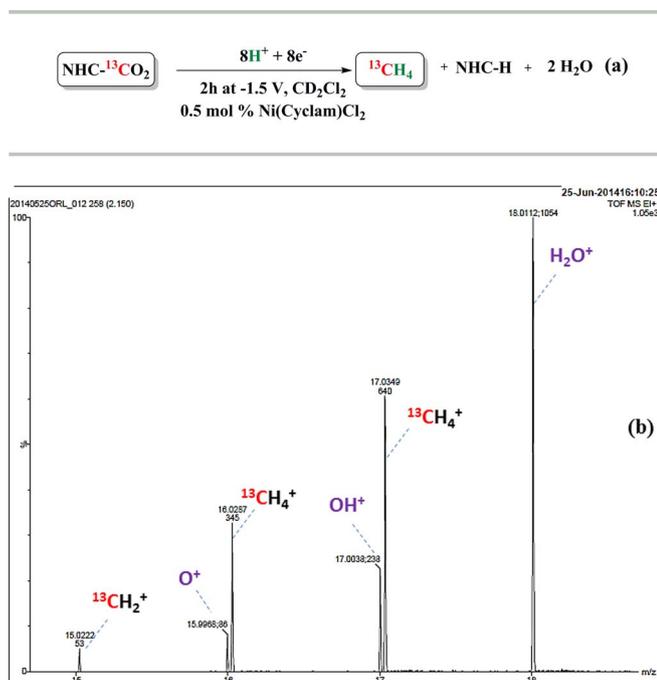


Figure 3. ¹³C Labeling experiments for the reduction of NHC-CO₂-¹³C. (a) Chemical equation for the ¹³C-labeling experiment in the selective electrochemical conversion of CO₂ to methane. (b) Water-resolved mass spectrum of an electrolysis headspace sample for the ¹³C-labeling experiment.

mass. ¹³CH₃⁺ appears at an intensity consistent with electron impact library mass spectra of methane, and is 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 ¹³CH₃⁺ 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 trifluoromethanol 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 ¹³CD₄ (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)]²⁺, 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 potentiostat/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 *n*Bu₄NBF₄) separated from the solution by a Vycor frit (Bioanalytical Systems, Inc.) and externally referenced to ferrocene. We report the potentials vs Ag/AgNO₃, but we also provide an alternate Fc/Fc⁺ 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 K_α1,2 (hν = 1486.6 eV) operating at 30 mA and 15 kV.^{28,29}

Additional details are available in the Supporting Information.

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