

Communication

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Yanwei Lum, Tao Cheng, William A. Goddard, and Joel W. Ager

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Electrochemical CO reduction builds solvent water into oxygenate products

Yanwei Lum^{†,‡,⊥}, Tao Cheng^{§,},,, William A. Goddard III^{*,§,} and Joel W. Ager^{*,†,‡}

[†]Joint Center for Artificial Photosynthesis and Materials Sciences Division, Lawrence Berkeley National Laboratory, California 94720, United States.

[‡]Department of Materials Science and Engineering, University of California, Berkeley, California 94720, United States.

[§]Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, California 91125, United States.

^{II}Materials and Process Simulation Center (MC139-74), California Institute of Technology, Pasadena, California 91125, United States.

Supporting Information Placeholder

ABSTRACT: Numerous studies have examined the electrochemical reduction of CO (COR) to oxygenates (e.g. ethanol). None considered the possibility that oxygen in the product might arise from water rather than from CO. To test this assumption, C¹⁶O reduction was performed in H₂¹⁸O electrolyte. Surprisingly, we find that **60-70% of the ethanol has** ¹⁸O, which must originate from the solvent. We extended our previous all solvent density functional theory metadynamics calculations to consider the possibility of incorporating water, and indeed we find a new mechanism involving a Grotthuss chain of six H₂Os in a concerted reaction with the *C-CH intermediate to form *CH-CH(¹⁸OH), subsequently leading to ¹⁸O ethanol. This competes with the formation of ethylene that also arises from *C-CH. These unforeseen results suggest that all previous studies of COR under aqueous conditions must be reexamined.

Electrochemical CO₂ reduction (CO₂R) has emerged as a promising technology to utilize increasingly cheaper renewable electricity to convert CO₂ into useful chemicals and fuels.¹⁻⁶ In this context, Cu-based catalysts are currently the most promising for driving CO₂R to produce significant amounts of multicarbon oxygenates and hydrocarbons such as ethanol and ethylene.⁷⁻¹⁰ Enabling the deterministic design of more selective and efficient catalysts requires understanding of the reaction mechanisms to predict how changes in the catalysts and electrolyte can modify the kinetics and products. Indeed, a number of theoretical papers have been published explaining how the experimentally observed changes in products depend on pH, applied potential, and presence of counter ions.¹¹⁻¹⁴ It is generally accepted that on various Cu surfaces, CO₂ reduces first to CO.^{15,16} Åt low pH, CO can further reduce to *HCO or *OCH and then to *CH2OH, leading to methane or methanol formation.^{14,17} At pH> 7, CO can undergo C-C coupling to generate a *CO-CO dimer,^{14,17–21} which then forms *OC-COH.²² Subsequent steps leading to ethylene and ethanol have been further studied in quantum mechanics (QM) based theory papers.^{17–19,23–25}

Recently, we published the first complete determination of the atomistic reaction mechanism for reduction of CO on Cu (100) using QM based metadynamics in full solvent to determine the free-energy barriers and kinetics at 298 K.¹⁸ We showed that sol-

vent water on the Cu surface plays an essential role in the mechanisms by providing hydrogen to the intermediates and products. This role of surface water, which involves transferring hydrogen to these intermediates, often through a Grotthuss mechanism involving other solvent waters, was a new result. In our previous QM calculations¹⁸ for CO reduction on Cu, we found that the pathway for ethanol formation proceeds through *(OH)C-CH; an intermediate after 4 e^{-} transfers, which then subsequently either reduces to *C-CH (leading to ethylene formation with a free energy barrier of 0.61 eV) or to *H(OH)C-CH (leading to ethanol with a free energy barrier of 0.67 eV). However, we did not consider the possibility that solvent water could provide the O in the products, and we assumed that all the O atoms in the oxygenate $(C_nH_mO_x)$ products come from the original CO molecule being reduced. In fact, this is a common feature of all current proposed mechanisms, with recent work from Head-Gordon and co-workers predicting that none of the oxygenate products should possess oxygen from the solvent water.23

We tested this critical assumption experimentally by carrying out reduction of $C^{16}O$ in $H_2^{18}O$ electrolyte on various Cu surfaces and quantifying the isotopic composition of the products using gas chromatography-mass spectrometry (see SI for more details). An important reason that CO reduction and not CO2 reduction was performed is because CO₂ is known to rapidly equilibrate with water to form bicarbonate.²⁶ Therefore, dissolved CO_2 would likely incorporate ¹⁸O from the solvent, resulting in ¹⁸O in the products. In contrast, CO does not exchange O with water (see SI for more details). The reduction of $C^{16}O$ in 0.05 M K₂CO₃ (pH 11.3) electrolyte was carried out with different Cu orientations: Cu (111), Cu (100) and Cu (751) at a potential of -0.64 V vs RHE. Analysis of the isotopic composition of the products (Figure 1a) reveals that the majority of the ethanol, acetate and 1-propanol are ¹⁸O enriched. In order to ensure that incorporation of ¹⁸O into the products were not solely due to homogenous reactions occurring in the bulk of the electrolyte (e.g. Cannizzaro reactions²⁷), a series of control experiments were conducted (see SI for more details). Control experiments were also performed to ensure that the mass spectrometer has similar detection sensitivities for ¹⁶O vs ¹⁸O fragments (see SI for more details).

For all three Cu surfaces, the fraction of ethanol with ¹⁸O is around 66% and that for 1-propanol is around 72%. Acetate possesses 2 oxygen atoms and therefore may have 3 different config-

urations: ¹⁶O¹⁶O, ¹⁶O¹⁸O and ¹⁸O¹⁸O acetate. ¹⁸O¹⁸O acetate was not observed on any of the Cu surfaces and the distribution of ¹⁶O¹⁶O versus ¹⁶O¹⁸O depends on the Cu orientation, with Cu (100) producing the highest fraction of ¹⁶O¹⁸O (>90%). Additionally, allyl alcohol (prop-2-en-1-ol) was detected as a product on all surfaces and methanol only on the Cu (111) surface. Interestingly, **allyl alcohol and methanol were not enriched with** ¹⁸**O**, which suggests that the mechanisms for their formation may be very different. These findings are summarized in a chart in Figure 1b, which sorts the products into those with ¹⁸O and those without ¹⁸O.



Figure 1. Fraction of product with ¹⁸O for ethanol (red), acetate (yellow) and 1-propanol (green) for $C^{16}O$ reduction in $H_2^{18}O$ electrolyte with: (a) different Cu orientations tested at c.a. -0.65V vs RHE, (c) Cu (100) at different pH and (d) Cu (100) at different applied potentials. (b): A chart showing products with an ¹⁸O pathway (ethanol, acetate and 1-propanol) and products without an ¹⁸O pathway (methanol and allyl alcohol). Note: ¹⁸O¹⁸O acetate was never observed as a product. Faradaic efficiency data are available in the SI.

Next, the effect of pH and potential was investigated for the Cu (100) surface. A potential of around -0.53V vs RHE was applied at different pH; 11.3 (0.05 M K₂CO₃), 13 (0.1 M KOH) and 14 (1.0 M KOH). Figure 1c shows that changing the pH has no effect on the ¹⁸O composition of ethanol, which remains at around 64%. On the other hand, the ¹⁸O composition of acetate and 1-propanol are significantly affected by pH. For 1-propanol, the ¹⁸O composition rises from 73% at pH 11.3 to 91% at pH 14. However, for acetate, the ¹⁶O¹⁸O composition decreases from 90% at pH 11.3 to 66% at pH 14. Keeping the pH constant at 11.3 and changing the potential (Figure 1d) has no effect on the isotopic composition of the products. Additionally, changing the potential or pH does not result in any ¹⁸O¹⁸O acetate formation.

Summarizing the experiments, by using ¹⁸O labeling of the solvent we have discovered that that the majority of the ethanol, acetate and 1-propanol produced by COR on single crystal Cu surfaces possess ¹⁸O, **showing conclusively that solvent water plays a dominant role in their formation**. As a result of this unexpected finding, all previous mechanisms for the formation of $C_nH_mO_x$ oxygenates require reexamination because H₂O as the dominant source of O for the formation of these products has been overlooked.

Stimulated by the experimental results, we used quantum mechanics (QM) metadynamics in with full solvent (5 layers) to determine the free energy barriers at 298 K to investigate how $H_2^{18}O$ (solvent) could contribute ¹⁸O to the product. The experimental results clearly demonstrate the existence of two ethanol formation pathways (¹⁶O pathway and ¹⁸O pathway). Therefore, the $H_2^{18}O$ must react with a C₂ intermediate which has lost both its oxygen atoms: either *C-CH, *C-CH₂ or *HC-CH₂. We considered that the most plausible C₂ intermediate to react with ¹⁸O water is adsorbed ethynyl (*C-CH).

Thus, we explored the possibility of a two-step *CH-CH(¹⁸OH) formation:

- First, one surface H₂¹⁸O might provide a proton (H⁺) to form *HC-CH plus surface ¹⁸OH (*¹⁸OH) via proton-coupled electron transfer (PCET).
- Second, this might be followed by *¹⁸OH extracting an H⁺ from a solvent H₂¹⁸O to deliver the ¹⁸OH to form *CH-CH(¹⁸OH) via PCET.

However, the free energy barrier for the first step is 1.09 eV while the that for the 2nd step is 1.22 eV. These barriers are much larger than the values of 0.61 and 0.67 eV that we found previously to produce ethene and ethanol. Thus we conclude that this mechanism does not explain the large amount of ¹⁸O ethanol observed.

We then investigated a concerted pathway of water addition reaction via Grotthuss water chain in which the water at C end provide H^+ to C (in *C-CH) while water at CH end simultaneously providing ¹⁸OH⁻ to CH (in *C-CH) which are connected by the

hydrogen bond network through bridging water molecules. We considered several possible such chains with the best involves 6 water molecules, leading to a free energy reaction barrier for this reaction of 0.81 eV. We also examined this reaction for chemisorbed ethyne (*HC-CH) to form *CH₂-CH(¹⁸OH) and we find a slightly higher barrier of 0.84 eV. Finally, we also examined the reaction where *C-CH (ethynyl) forms *C(¹⁸OH)H-CH, where we find a barrier of 0.91 eV. Thus, we distinguish the formation of *CH-CH(¹⁸OH) from *C-CH via water addition as the most possible mechanism attributes to C₂H₅(¹⁸OH) formation, which we refer as Grotthuss Chain Ethynyl Concerted Hydrolysis (GECH), a most unexpected and unprecedented reaction which has never been reported before. The critical steps of such unprecedented non-electrochemical reaction from QM metadynamics snapshots are as shown in Figure 2 (see also supplementary movie 1)."

After the formation of *CH-CH(¹⁸OH) from *C-CH via water addition, the remaining steps toward $C_2H_5(^{18}OH)$ formation and the related energetics are as shown in Figure 3. GECH is expected to be independent of pH and applied potential. In the SI, we report a simulation with explicit consideration of 1 M NaOH (pH = 14) where we found the free energy barrier of 0.87 eV, supporting this claim. The experimental results in Figures 1c and d do not show a large dependence on either pH or potential, supporting our claim the GECH is responsible for the formation of ^{18}O ethanol.



Figure 2. The reactive trajectory for Grotthuss Chain Ethynyl Concerted Hydrolysis (GECH) the of *C-CH to *CH-CH(OH) from full solvent quantum mechanics molecular metadynamics free energy calculations. All the 6 waters in the Grotthuss chain are shown in full. The other **48** water molecules not involved in the chain are faded out for clarity. This intermediate CH-CH(OH) subsequently forms ethanol as shown in the orange pathway in Figure 3. We examined a number of possible pathways involving various numbers of waters, with this being the most favorable. (a) initial reactants, (b) transition state (free energy barrier: 0.81 eV) and (c) final products (exothermic by - 0.12 eV). The colors are C in gray, O in red, the H involved in the Grotthuss chain proton transfer) are in yellow, and other H are white.

Since *(¹⁶OH)C-CH is a common intermediate for forming either ¹⁶O ethanol or to the sum of ethylene and ¹⁸O ethanol (see Figure 3), the predicted energy barriers at 298 K (0.67 and 0.61 eV respectively) can be used to estimate the ratio of the sum of ethylene plus ¹⁸O ethanol product to ¹⁶O ethanol. Based on the Arrhenius equation, this ratio was calculated to be 11 which is in excellent agreement with our experiments, which yield a ratio of 14 and a calculated energy difference in barriers of 0.066 eV (see Figure S28 for calculation details). Similarly, *C-CH is a common intermediate for forming both ¹⁸O ethanol and ethylene and the predicted activation energies at 298K (0.81 and 0.61 eV) can be compared to the observed ratio of 0.15, which implies that the difference in barriers is 0.049 eV. This difference in experiment and theory suggests that we may not have exhausted on all the pathways for the GECH mechanism.



Figure 3. The mechanistic pathways for CO reduction predicted from full solvent quantum mechanics based molecular metadynamics to obtain free energy reaction barriers at 298K. The pathways of ethylene formation (black) and ¹⁶O ethanol (blue) are from ref 18. The ¹⁸O ethanol formation pathway (orange) is a newly discovered mechanism (GECH) reported here.

In summary, our QM based metadynamics show that ¹⁸O ethanol results from a solvent based concerted hydrolysis of *C-CH (chemisorbed ethyne) to *CH-CH(OH), in which the added H and OH are derived from waters at the opposite ends of a 6 molecule Grotthuss chain (GECH). This is a brand-new mechanism, which is independent of pH and applied potential and may provide new approaches to designing nanoscale structures and compositions in which the energy and orientation of the chemisorbed ethynyl intermediates are used to promote the solvent water induced ethanol or other $C_nH_mO_x$ oxygenate products.

In this work, the main focus was to understand the formation of ¹⁸O ethanol was because it is the most abundant ¹⁸O oxygenate produced. Subsequent work will examine the C₃ product pathways for 1-propanol and allyl alcohol formation as well as the acetate pathways, which are evidently more complicated. Since we now know that incorporation of ¹⁸O is critical in the formation of oxygenates, it is paramount to use this technique to investigate other catalyst systems used for COR such as bimetallic systems and oxide-derived Cu.^{28–32} For example, oxide-derived Cu catalysts have been shown to yield a high selectivity towards oxygenates versus hydrocarbons.³¹ It is expected that such experiments will lead to new insights on how oxygenate formation mechanisms might be different on these catalysts. Finally, our discovery of concerted solvent water incorporation of O into oxygenates may have implications for many other oxygen insertion processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Synthesis, characterization, experimental methods and control experiments.

AUTHOR INFORMATION

Corresponding Author

- * wag@wag.caltech.edu
- * jwager@lbl.gov

Author Contributions

[⊥]These authors contributed equally.

Notes

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