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Electrochemical CO reduction builds solvent water into oxygenate products

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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, C\textsuperscript{18}O reduction was performed in H\textsubscript{2}O electrolyte. Surprisingly, we find that 60-70\% of the ethanol has \textsuperscript{18}O, 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 Grothuss chain of six H\textsubscript{2}O\textsubscript{m} in a concerted reaction with the *CH\textsubscript{2}OH intermediate to form \textsuperscript{18}O ethanol. This competes with the reaction of ethylene that also arises from *CH\textsubscript{2}OH. These unforeseen results suggest that all previous studies of COR under aqueous conditions must be reexamined.

Electrochemical CO\textsubscript{2} reduction (CO\textsubscript{2}R) has emerged as a promising technology to utilize increasingly cheaper renewable electricity to convert CO\textsubscript{2} into useful chemicals and fuels.\textsuperscript{1-6} In this context, Cu-based catalysts are currently the most promising for driving CO\textsubscript{2}R to produce significant amounts of multicomponent oxygenates and hydrocarbons such as ethanol and ethylene.\textsuperscript{7-16} Enabling the deterministic design of more selective and efficient catalysts requires understanding of the reaction mechanisms to predict how changes in the catalyst 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.\textsuperscript{11-14} It is generally accepted that on various Cu surfaces, CO\textsubscript{2} reduces first to CO.\textsuperscript{15,16} At low pH, CO can further reduce to \textsuperscript{18}HCO or \textsuperscript{18}OCH and then to \textsuperscript{18}CH\textsubscript{2}OH, leading to methane or methanol formation.\textsuperscript{14,17} At pH > 7, CO can undergo C-C coupling to generate a *CO-CO dimer,\textsuperscript{14,17-21} which then forms \textsuperscript{18}OC-COH.\textsuperscript{22} Subsequent steps leading to ethylene and ethanol have been further studied in quantum mechanics (QM) based theory papers.\textsuperscript{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.\textsuperscript{18} We showed that solvent 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 Grothuss mechanism involving other solvent waters, was a new result. In our previous QM calculations\textsuperscript{18} for CO reduction on Cu, we found that the pathway for ethanol formation proceeds through *H(OH)C-CH; an intermediate after 4 e\textsuperscript{-} 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\textsubscript{2}H\textsubscript{4}O\textsubscript{m}) 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.\textsuperscript{25}

We tested this critical assumption experimentally by carrying out reduction of C\textsuperscript{18}O in H\textsubscript{2}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 CO\textsubscript{2} reduction was performed is because CO\textsubscript{2} is known to rapidly equilibrate with water to form bicarbonate.\textsuperscript{26} Therefore, dissolved CO\textsubscript{2} would likely incorporate \textsuperscript{18}O from the solvent, resulting in \textsuperscript{18}O in the products. In contrast, CO does not exchange O with water (see SI for more details). The reduction of C\textsuperscript{18}O in 0.05 M K\textsubscript{2}CO\textsubscript{3} (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 \textsuperscript{18}O enriched. In order to ensure that incorporation of \textsuperscript{18}O into the products were not solely due to homogeneous reactions occurring in the bulk of the electrolyte (e.g. Cannizzaro reactions\textsuperscript{27}), 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 \textsuperscript{18}O vs \textsuperscript{16}O fragments (see SI for more details).

For all three Cu surfaces, the fraction of ethanol with \textsuperscript{18}O is around 66\% and that for 1-propanol is around 72\%. acetate possesses 2 oxygen atoms and therefore may have 3 different config-
Next, the effect of pH and potential was investigated for the Cu (100) surface. A potential of around -0.53 V vs RHE was applied at different pH: 11.3 (0.05 M K$_2$CO$_3$), 13 (0.1 M KOH) and 14 (1.0 M KOH). Figure 1c shows that changing the pH has no effect on the $^{18}$O composition of ethanol, which remains at around 64%. On the other hand, the $^{18}$O composition of acetate and 1-propanol is significantly affected by pH. For 1-propanol, the $^{18}$O composition rises from 73% at pH 11.3 to 91% at pH 14. However, for acetate, the $^{16}$O 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 $^{18}$O/16O acetate formation.

Summarizing the experiments, by using $^{18}$O labeling of the solvent we have discovered that the majority of the ethanol, acetate and 1-propanol produced by COR on single crystal Cu surfaces possess $^{16}$O, 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$_n$H$_{2n+1}$O$_x$ oxygenates require reexamination because H$_2$O 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 $^{18}$O to the product. The experimental results clearly demonstrate the existence of two ethanol formation pathways ($^{16}$O pathway and $^{18}$O pathway). Therefore, the H$_2^{18}$O must react with a C$_2$ intermediate which has lost both of its oxygen atoms: either *C-CH, *C-CH$_2$ or *HC-CH$_2$. We considered that the most plausible C$_2$ intermediate to react with $^{18}$O water is adsorbed ethynyl (*C-CH).

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

1. First, one surface H$_2^{16}$O might provide a proton (H$^+$) to form *HC-CH plus surface $^{18}$OH via proton-coupled electron transfer (PCET).
2. Second, this might be followed by $^{18}$OH extracting an H$^+$ from a solvent H$_2^{18}$O to deliver the $^{16}$O to form *CH-CH($^{16}$OH) 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 $^{18}$O ethanol observed.

We then investigated a concerted pathway of water addition reaction via Grothuss water chain in which the water at C end provide H$^+$ to C in *C-CH while water at CH end simultaneously providing $^{18}$OH$^-$ to CH in *C-CH which is 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 C2H5(18OH) 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 18O 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 *H(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 \textsuperscript{18}O ethanol results from a solvent based concerted hydrolysis of \textsuperscript{18}C-CH (chemisorbed ethyne) to \textsuperscript{18}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\textsubscript{n}H\textsubscript{2n+1}O oxygenate products.

In this work, the main focus was to understand the formation of \textsuperscript{18}O ethanol because it is the most abundant \textsuperscript{18}O oxygenate produced. Subsequent work will examine the C\textsubscript{3} 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 \textsuperscript{18}O 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\textsuperscript{2+}-\textsuperscript{32} For example, oxide-derived Cu catalysts have been shown to yield a high selectivity towards oxygenates versus hydrocarbons.\textsuperscript{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.

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Notes
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REFERENCES
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