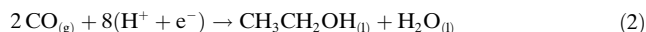
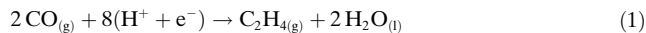


Theoretical Considerations on the Electroreduction of CO to C₂ Species on Cu(100) Electrodes**

Federico Calle-Vallejo and Marc T. M. Koper*

The electroreduction of CO₂ or CO to hydrocarbons and other related compounds on Cu electrodes has attained remarkable interest since its discovery.^[1] Most of the studies devoted to understanding its reaction mechanism have been experimental,^[1e,f,2] while theoretical insight has been provided recently for the formation of C₁ species, such as CH₄, CO, and HCOOH.^[3] This reaction offers the possibility of transforming carbon oxides into fuels for automotive applications (CH₄ and ethanol (EtOH)) and raw materials with wide and important industrial uses (C₂H₄). In the electrochemical environment of this reaction, that is, abundant protons and negative electrode polarization, diverse catalytic behaviors are observed: Ni, Fe, Pt, and Ti cathodes produce H₂ and no CO/CO₂ is reduced. Post-transition metals, such as Pb, In, Sn, and Tl mostly produce formate. Additionally, Au, Ag, Zn, and Pd reduce CO₂ only to CO. Cu has the exceptional ability to reduce CO₂/CO to CH₄, C₂H₄, EtOH, and a variety of other products.^[1f,4] However, the large overpotentials hinder global spread of this technology.^[1a] Thus, before any technical considerations on the implementation of electrolytic cells for CO₂/CO reduction are made, the fundamental problem of the electrocatalysis at the cathode must be solved. The first step towards an optimized performance is evidently the formulation of a mechanism able to explain the observed product distribution, the onset potentials, and the effect of different electrode facets and electrolyte concentrations on the catalytic activity. Herein we present a mechanism for the production of C₂H₄, EtOH, and acetaldehyde (MeCHO) from CO on Cu(100) electrodes. This facet has been reported to be particularly selective towards C₂H₄ production, with EtOH and MeCHO as C₂ side products.^[1d] Another striking observation is that on Cu(100), C₂ products are formed at low overpotentials without the formation of C₁ products.^[2b]

We will show that a mechanism that can explain the experimental observations on Cu(100) should have a rate-determining step (RDS) consisting of the coupling of two CO molecules mediated by electron transfer to form *C₂O₂. This dimer is transformed into C₂H₄ and EtOH by proton–electron transfer, according to the following overall reactions [Eq. (1) and (2)]:



The adsorption energies, which include various corrections and appear in the Supporting Information, are calculated relative to CO (g) and (H⁺ + e[−]), using the Computational Hydrogen Electrode^[5] (CHE) model in the way explained in the Supporting Information. The calculated onset potential of the reaction is the smallest applied potential *U* needed to make all steps exergonic, that is, the potential for which the free energies of all elementary reactions of a given pathway are negative or zero. The potential-determining step (PDS) of a given pathway is defined as the last step to become exergonic when the potential is modified.^[3b,6] This model is purely thermodynamic and assumes that the kinetic barriers of uphill processes are not much larger than their reaction energies and that downhill processes have easily surmountable barriers.^[3b] It has been shown theoretically that the barriers for proton transfer during the oxygen reduction can easily be overcome as they are approximately 0.15–0.25 eV,^[7] and no double or triple bonds are entirely broken in a single step in the pathways found.

Figure 1 shows the lowest-overpotential pathways for the CO reduction to C₂H₄, MeCHO, and EtOH. Schematic representations of the intermediates are given in Figure 2. The energetic levels of all the species are given at *U* = 0 V_{RHE} (RHE = reversible hydrogen electrode) and at a calculated onset potential of −0.40 V_{RHE}. This value is close to the one commonly accepted.^[1a]

C–C bond lengths are useful to track the presence of multiple bonds in the intermediates. According to the energies provided in the Supporting Information, *COCHO, precursor of for example, glyoxal, is less stable than *CO-COH by 0.16 eV, suggesting a more favorable initial hydrogenation of the O atoms in *C₂O₂. *CO-COH has a C–C bond length of 1.46 Å, different from the values of 1.29 and 1.33 Å found in gas-phase for C₂O₂ and C₂H₄, indicating the existence of a single C–C bond. The alternatives for the hydrogenation of *CO-COH are *CCO + H₂O, precursor of C₂H₄, and *OHCCOH, *OHCCHO, and *OHCHCO, precursors of ethylene glycol and glycolaldehyde. We find that the route towards ethylene is thermodynamically favored by at least 0.75 eV. These results help explain why Kuhl et al.^[1f] and Hori et al.^[1a,e] found that the yields of all C₂ compounds other than ethanol and ethylene are below 1 % and have high onset potentials. Chemically speaking, the ease of protonation and subsequent dehydration of OH groups makes them more reactive in reducing environments than O atoms in carbonyl

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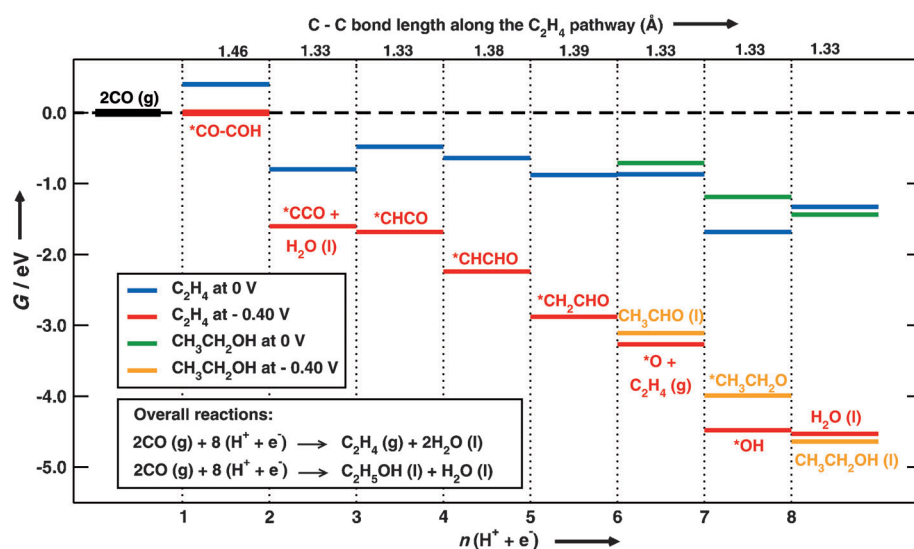


Figure 1. Lowest energy pathways for the electroreduction of CO to C₂H₄, MeCHO/EtOH at 0 V (blue, green) and –0.40 V (red, orange). The PDS is the first proton–electron transfer. C–C bond lengths are given in the upper x-axis for the pathway to C₂H₄.

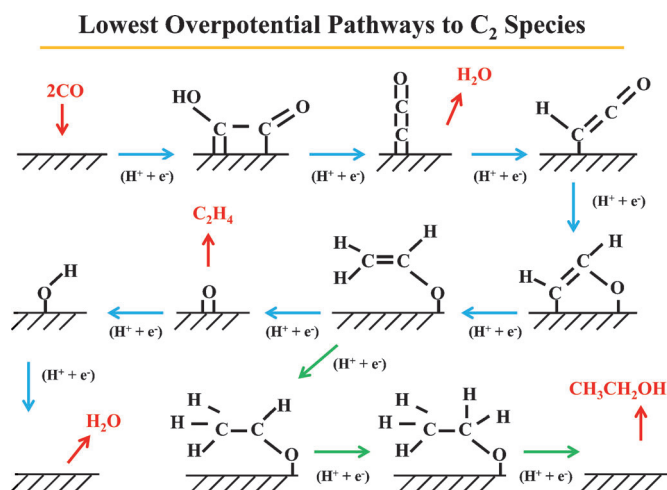


Figure 2. Schematic representations of the species involved in the pathways to C₂H₄ (blue) and MeCHO/EtOH (green).

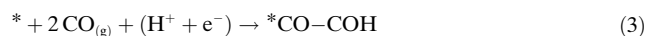
groups, this being the reason why H₂O is desorbed in the next step leaving an adsorbed *CCO group.^[8] *CCO has a C–C bond length of 1.33 Å, typical of C=C double bonds. From this point on, the subsequent proton–electron additions proceed such that the C–C double bond is preserved: the next step is an α -carbon protonation (*CHCO), followed by a protonation of the C atom in the carbonyl group (*CHCHO). This oxametallacycle binds to the surface through both C and O and has a C–C bond length of 1.39 Å. In the next step another protonation in the α -carbon takes place, producing *CH₂CHO. The next proton–electron transfer is rather important because in it the pathway to MeCHO/EtOH splits from that to C₂H₄ (See Figure 1 and 2). The C₂H₄ pathway proceeds with protonation of the C atom bonded to the O atom, resulting in the transient formation of

*CH₂CH₂O. The C–O bond is rapidly cleaved and C₂H₄ is desorbed, leaving an *O adsorbate. *O is hydrogenated to *OH and then to H₂O. Alternatively, MeCHO is formed by protonation of the α -carbon in *CH₂CHO. Furthermore, MeCHO reduction to EtOH occurs via an ethoxy intermediate (*CH₃CH₂O). In case the thermodynamically unlikely hydrogenation of *CH₂CHO to give vinyl alcohol (CH₂CHOH (g)) occurs, this unstable product would instantly tautomerize to MeCHO.^[14,9]

The fact that C₂H₄, MeCHO, and EtOH share the same pathway up to the fifth electrochemical step helps explaining some experimental features of the CO/CO₂ reduction. It is observed that C₂H₄ is the most abundant C₂ product (40.7% of current efficiency), followed by EtOH (12.8%) and MeCHO (1.0%) at a potential of –1.39 V_{SHE} (SHE = Standard hydrogen electrode).^[14] The proportion between EtOH and C₂H₄ can be rationalized qualitatively in terms of the favorability of the sixth hydrogenation step, which is inclined towards C₂H₄ formation by approximately 0.2 eV, but this should be corroborated by kinetic studies like those in Ref. [10]. The low yield of MeCHO is also the result of its further reduction to EtOH. It is important to consider the observations of Murata and Hori,^[11] who found that the presence of different alkaline cations, that is, Li⁺, Na⁺, K⁺, and Cs⁺, affected the product selectivity of the CO/CO₂ reduction on Cu electrodes. Interestingly, they observed that these cations influenced the formation of C₂H₄ and EtOH in identical ways, indicating that they are formed in the same pathway. Recently, Kuhl et al.^[14] concluded that the presence of hydroxy and carbonyl groups in several C₂ and C₃ products of the CO₂ reduction is an indication of an early C–C coupling step, occurring before the cleavage of at least one of the C–O bonds in CO₂.

Another interesting experimental observation is that ethylene oxide (C₂H₄O) can be readily reduced to C₂H₄ at potentials lower than those required to reduce CO.^[2a] The lowest-energy pathway for this reaction is given in Figure S5. The only uphill step is the clearance of *OH from the surface, which is predicted to start at –0.33 V. It can be inferred from Figure 1 and Figure S5 that adsorbed ethylene oxide (*CH₂CH₂O) is an intermediate of the reduction of both CO and C₂H₄O and that its dissociation into C₂H₄ (g) and *O is a thermodynamically favorable step, with a free energy change of approximately 0.4 eV. This situation confirms the conclusions of Schouten et al.,^[2a] who suggested that adsorbed ethylene oxide might be a reaction intermediate of the CO reduction.

We draw our attention now to the first electrochemical step in Figure 1. The reaction is given in Equation (3).



In it, two CO molecules are coupled through their C atoms and one of the O atoms is hydrogenated. In the following, we will argue that Equation (3) is a reaction in which electron and proton transfer are effectively decoupled, and consists of three subsequent processes (see Figure 3a): 1) CO adsorp-

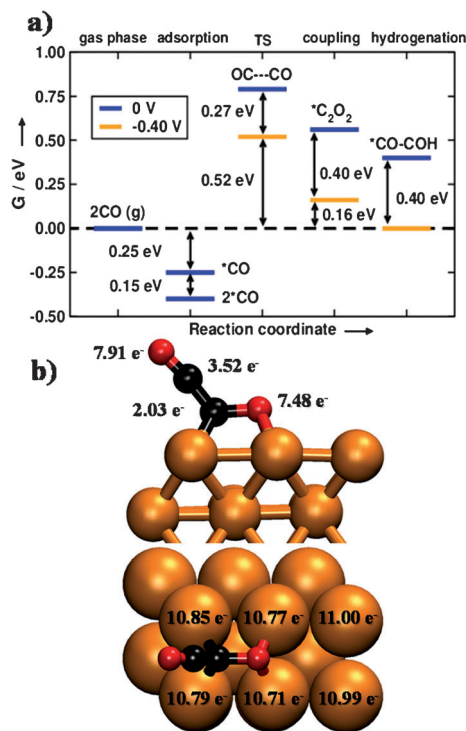


Figure 3. a) Deconvolution of the first electron–proton transfer at 0 V and –0.40 V. b) Adsorption geometry and Bader charges of the dimer and the surface. C black, O red.

tion; 2) coupling of *CO with CO(g) via electron transfer to form *C₂O₂[–]; 3) protonation of *C₂O₂[–] to form *CO–COH. The reactions are given in Equations (4)–(6).



The CHE model predicts that at –0.40 V the overall reaction [Eq. (3)] will be thermodynamically feasible, provided that the reaction energies of uphill processes and barriers are similar, which is the case in Figure 3a, where the free energies of *C₂O₂[–] and its transition state and *CO–COH are close to each other at 0 V, within the accuracy of standard DFT. The decoupling of proton and electron transfer in Equation (3) explains a remarkable experimental observation of the CO reduction: while CH₄ formation depends on the pH value on the SHE scale, suggesting concerted proton–electron transfer, there is no influence of pH value on C₂H₄

formation on Cu(100).^[1a,c,2a] This situation suggests that the rate-determining step happens at an early stage of the mechanism and that there should be no proton transfer involved in that step or in the ones before it.^[2a] Thus, the only constraint in our search for the lowest-overpotential pathways was that C–C coupling should happen before the first proton transfer, and the fact that this step is found to be the PDS is purely an outcome of the calculations.

In favor of our hypothesis, we remark that in the general theory of proton-coupled electron transfer, such a decoupling will happen if the intermediate has a high electron affinity.^[12] This is exactly the case for the dimer, as C₂O₂[–] and C₂O₂^{2–} are more stable^[13] than C₂O₂^[14] (see also Figure S1), implying a favorable electron affinity of the dimer. Hori et al.^[15] have argued that CO adsorption on Cu electrodes may be mediated by electron transfer, and did not observe this feature on other metals. Furthermore, in organic chemistry it is established that C–C coupling may occur through reductive CO coupling, in a reaction known as McMurry coupling, in which charged species or free radicals are involved.^[8] From that perspective, after the electron transfer O acts as a strong nucleophile and reacts readily with H⁺, forming an OH group and neutralizing the charge to form *CO–COH. Another argument in favor of the CO coupling under electrochemical conditions is found in experiments by Bard et al.,^[16] who reduced CO in an aprotic solvent (liquid ammonia) to C₂O₂^{2–} on Pt, Ni, C, and Hg electrodes at highly negative potentials. In the Supporting Information we show that while the calculated association enthalpy (ΔH) and its corresponding activation energy (E_a) for CO in gas phase to form C₂O₂ are high, 1.42 and 4.48 eV, the coupling through a charge-transfer mediated process to give C₂O₂[–] is evidently easier. Such process has a ΔH of –0.19 eV, implying a more favorable configuration of C₂O₂[–] (i.e. a favorable electron affinity) with respect to C₂O₂ and E_a ≈ 0.6 eV, which is a reasonably surmountable barrier. Note that the addition of an electron decreases ΔH by approximately 1.5 eV and E_a by approximately 4 eV with respect to the charge-neutral situation.

Further support for our hypothesis is given in Figure 3b. It contains the adsorption geometry of the most stable dimer found in our calculations and the corresponding Bader^[17] charges of the surface atoms. *C₂O₂[–] binds through both O and C to four Cu atoms. The number of valence electrons of the Cu atoms in the slab (and those in the layers below) which do not couple to the dimer is approximately 11, as expected. However, that number is approximately 10.75 for the other four Cu atoms, meaning that there is 1 e[–] less at the surface. Conversely, the sum of the electrons of the dimer is approximately 21 e[–], one more than expected, as C has 4 valence electrons and O has 6. Hence, the dimer is negatively charged in its adsorbed state and we expect that it will be additionally stabilized by solvation effects (the extra charge on the dimer at the transition state is ca. 2/3 e[–], see the Supporting Information, which justifies the drop of 0.27 eV in the barrier at –0.40 V). The extra charge is located in the CO moiety that does not couple to the surface, which may allow further coupling to create the C₃ species observed by Kuhl et al.^[1f] Note that the adsorption geometry in Figure 3b would explain why Cu(100) is such an active surface for this

reaction.^[2b] Based on all the aforementioned observations, we propose the dimer formation on Cu(100) to occur by a sequential electron–proton transfer.

The mechanism with a rate-determining CO coupling step explains a number of experimental observations that other recent DFT-based models for C–C coupling in CO electroreduction cannot reproduce.^[1a,18] It naturally explains why on Cu(100) at low overpotential only C₂ products and not C₁ products are observed, whereas other models predict the simultaneous formation of CH₄ and C₂H₄. Secondly, the decoupling of proton–electron transfer in Equations (4)–(6), with the electron transfer being rate-determining, leads to a pH-independent C₂H₄ formation on the SHE scale, in agreement with experiments.^[1a,c] This important experimental observation is not explained by other C–C coupling models, which assume concerted proton–electron transfers at every step in the mechanism and proceed by C–C coupling of hydrogenated C moieties. In the Supporting Information we briefly discuss the effect of H coadsorption and CO coverage on the results shown herein. We note that further studies are required to improve Cu electrodes by, for example, alloying, or to identify new materials capable of reducing CO₂/CO at low overpotentials.

Experimental Section

All DFT simulations were made with the VASP code.^[19] Further details are given in the Supporting Information.

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