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Bicarbonate is Not a General Acid in Au-Catalyzed CO₂ Electrocatalysis

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Supporting Information Placeholder

ABSTRACT: We show that bicarbonate is neither a general acid nor a reaction partner in the rate-limiting step of CO₂ reduction catalysis mediated by planar polycrystalline Au surfaces. We formulate microkinetic models and propose diagnostic criteria to distinguish the role of bicarbonate. Comparing these models with the observed zero-order dependence in bicarbonate and simulated interfacial concentration gradients, we conclude that bicarbonate is not a general acid co-catalyst. Instead, it acts as a viable proton donor past the rate-limiting step and a sluggish buffer that maintains the bulk but not local pH in CO₂-saturated aqueous electrolytes.

The electroreduction of CO₂ would enable the storage of renewable sources of electricity in energy-dense carbonaceous fuels. CO₂ reduction reactions (CO₂RRs) require multiple proton-coupled electron transfer (PCET) steps, and thus control over fuel-formation rates and selectivities necessitates an understanding of the PCET pathways and the identification of the proton donor(s). CO₂RR is mostly conducted in aqueous electrolytes, where HCO₃⁻ exists by necessity because it is the product of CO₂ hydration. There is a consensus that HCO₃⁻ (and CO₃²⁻) is not directly reduced at the electrode surface, leaving open the question of whether bicarbonate acts as: (1) a general acid co-catalyst that directly participates in the rate-limiting step (RLS); and/or (2) simply a participant in electrolyte acid-base equilibria. Herein, we address this question in the context of the two-electron, two-proton reduction of CO₂ to CO catalyzed by polycrystalline Au surfaces.

The equilibrium values and reaction rates that govern (2) are well-established. CO₂ hydration to form bicarbonate presents an operative pH restriction for catalysis—only intermediate pH values are viable for CO₂RR in aqueous electrolytes due to the buffering point established by the CO₂-water-bicarbonate equilibrium. Fig. 1. Stopped-flow studies of CO₂ hydration and bicarbonate dehydroylation combined with femtosecond time-resolved infrared studies of carbonic acid generation demonstrate that while the rate of CO₂ hydration (Fig. 1, k₂ = 2.9 × 10⁻² s⁻¹) is slow, all other equilibria, including carbonic acid dissociation, are relatively fast. These rate constants suggest that CO₂ and bicarbonate equilibrate to buffer the pH in the bulk electrolyte. In addition, provided that the rate of CO₂RR catalysis does not outpace that of carbonic acid formation (k₃[OH⁻][HCO₃⁻]) and dehydroylation (k₄[H₂CO₃]), CO₂ can be replenished within the reaction diffusion layer proximal to the electrode surface via equilibrium proton transfer (PT) from buffer constituents. Indeed, a recent report using infrared and mass spectroscopies support CO₂ replenishment via these equilibria on the timescale faster than gas-liquid CO₂ mixing.

The answer to question (1), whether bicarbonate is an explicit reaction partner in the RLS of catalysis, remains the subject of debate. Computational and experimental studies invoke mechanisms for CO production that proceed via concerted proton electron transfer (CPET) to CO₂. Conversely, for planar polycrystalline Au electrodes, electrokinetic studies point to rate-limiting electron transfer (ET) and adsorption of CO₂ to form surface-bound COOH, but do not specify the identity of the proton donor, implying that H₂O⁺ and or H₂O act as general acids in the mechanistic sequence. In contrast, bicarbonate has been invoked as a general acid in mediating CO formation on oxide-derived polycrystalline Au electrodes. Conversely, for planar polycrystalline Au electrodes, electrokinetic studies point to rate-limiting electron transfer (ET) and adsorption of CO₂ to form surface-bound COOH, but do not specify the identity of the proton donor, implying that H₂O⁺ and or H₂O act as general acids in the mechanistic sequence. Further complicating the picture, bicarbonate has been recently proposed to not serve as a proton donor, but instead, as a reactant in a new equilibrium to form an anionic adduct of water, CO₂ and bicarbonate, denoted as I⁻. The adduct is proposed to be directly reduced at the electrode surface to form an adsorbed COOH intermediate. Additionally, studies of the role of bicarbonate are sometimes conducted in the presence of additional buffering ions, which themselves can promote or inhibit the reaction. The wide-ranging perspectives on the role of bicarbonate in fuel-forming catalysis motivate further mechanistic investigations.

Herein, we formulate diagnostic criteria for a series of possible mechanistic sequences that explicitly involve bicarbonate in or preceding the RLS of CO₂RR to form CO. We use electrokinetic data and stochastic reaction modeling to parse these competing mechanistic models and arrive at several viable possibilities.

In order to distinguish between various mechanistic pathways for CO production, we derived the expected current-potential (Tafel) behavior, CO₂ reaction order, and HCO₃⁻ reaction order for all previously proposed reaction sequences (Table 1). These theoretical Tafel slopes and reaction orders provide diagnostic criteria that can be compared with experimental data to down-select among viable mechanistic models. In order to thoroughly examine the possible role of HCO₃⁻, all mechanistic sequences deliberately invoke this anion as the proton donor in all PT and CPET steps. Analogous
In examining Table 1, we observe that assessing the role of bicarbonate prior to or in the RLS of CO$_2$RR to CO requires experimental identification of its reaction order coupled with the Tafel slope. Specifically, the electrochemical reaction order ($\rho$) in bicarbonate is defined by the partial derivative,

$$\rho = \frac{\partial \log j_{CO}}{\partial \log [\text{HCO}_3^-]}_{\text{CO}_2E},$$

which characterizes the dependence of the CO production rate or partial current density ($j_{CO}$) on the concentration of bicarbonate ([HCO$_3^-$]) in the electrolyte. For an irreversible electrochemical reaction, the reaction order is measured at a constant potential relative to a pH-independent reference electrode (E)\textsuperscript{rev.}.

We note that the reaction order can also be measured at constant overpotential ($\eta$), defined as the difference in $E$ and the reversible potential ($E_{\text{rev}}$). However, CO evolution on polycrystalline Au foils occurs far from $E_{\text{rev}}$ and, therefore, the overall reaction is irreversible under all conditions sampled. Thus, the rate expressions for the reaction can be most straightforwardly derived with respect to $E$, not $\eta$ (see SI). Under these irreversible conditions, reaction orders measured at constant $\eta$ are convoluted by the Tafel slope because the exchange-current density ($j_0$) in the Butler-Volmer equation is dependent not only on the concentration of species but also on the transfer coefficient for the overall reaction and $E_{\text{rev}}$.\textsuperscript{22} Furthermore, in most experiments, $E_{\text{rev}}$ at the electrode surface is subject to change as concentration gradients in reactants and products develop, see below, and these experimental variables can further convolute order data collected at constant $\eta$. We believe that this distinction between order data collected at constant $E$\textsuperscript{16,18} and $\eta$\textsuperscript{20} has been the source of inconsistencies in the literature.

Data collected under irreversible reaction conditions at constant $E$ reveal that polycrystalline Au electrodes (see SI and Fig. S1 for electrochemically active surface area measurements) display zero order dependence in bicarbonate for CO production, consistent with previous studies.\textsuperscript{18} The $j_{CO}$ was measured at applied potentials of −0.80 V, −0.90 V, and −1.00 V vs SHE (all potentials are referenced to the pH-independent Standard Hydrogen Electrode) spanning bicarbonate concentration values from 30 to 500 mM, Fig. 2a.
at bonate concentration dependence

Figure 2: Electrokinetic data for CO evolution catalysis. Bicarbonate concentration dependence (a) of partial current density at −0.80 V (black), −0.90 V (red), and −1.00 V (blue) vs SHE recorded in CO2-saturated bicarbonate electrolyte at constant 0.3 M ionic strength. Comparison of CO2RR conducted (b) 45 mM bicarbonate with (black) and without (red) 50 mM sodium phosphate. The [HCO3−] was varied at fixed ionic strength and constant sodium concentration by addition of sodium perchlorate, and the electrolytes were purified until voltammetric features associated with the oxidative stripping of Zn impurities were no longer observed following catalysis (Fig. S2). The use of Pt counter electrodes has been hypothesized to alter the Au working electrode surface structure over time via deposition of leached Pt, leading to the accumulation of irreversibly bonded CO species on the Pt/Au surface as a result of CO2RR. CO stripping analyses (see SI text and Figs. S3-S5) suggest that long-lived irreversibly-bound CO features persist on Au surfaces when employing Au counter electrodes, indicating that the presence of a Pt counter is insufficient to account for their existence. Nevertheless, studies discussed below use a Au counter electrode to eliminate the possibility of adventitious Pt deposition.

Data shown in Fig. 2a show that the concentration range probed, jCO is zero order in bicarbonate within error. Data were collected at E values where the reaction is known to exist under activation-control due to a lack of rotation-rate dependence on the measured current.18 We note that the pH changes from 6.2 to 7.2 as the bicarbonate concentration is altered from 30 to 300 mM at constant 1 atm CO2 partial pressure, however, jCO is independent of pH, see below, suggesting that the zero-order dependence observed is not due to equal and opposite bicarbonate and pH dependences18. In contrast to what we observe in Fig. 2a, previous studies have reported a 0.90 order in bicarbonate using phosphate (P1) as a coelectrolyte.2 In this study, the sum of the P1 and bicarbonate concentrations were fixed, meaning that p was extracted while simultaneously lowering the P1 concentration. Therefore, we postulate that this discrepancy may arise from an inhibitory role of P1, the attenuation of which would lead to the observed forward order in bicarbonate. To probe the dependence on P1 explicitly, we investigated the difference in jCO between CO2RR conducted in CO2-saturated 50 mM NaP1 (HCO3−−) = 45 mM) and CO2-saturated 45 mM NaHCO3 with 50 mM NaClO4 at applied potentials of −0.80 V to −1.00 V, Fig. 2b. The data shown in Fig. 2b highlights that P1 is a potent inhibitor of jCO on polycrystalline Au surfaces, and therefore convolutes reaction order studies conducted in this medium. Thus, we take the zero order dependence on bicarbonate measured in absence of P1, as the true reaction order.

The diagnostic criteria in Table 1 can only be compared with experimental reaction order data (Fig. 2a) if variations in the bulk concentrations of the relevant species correlate with changes in their concentration near the electrode surface. Steady-state mathematical modeling26–38 and experimental observations28,31–36 suggest a rise in the pH local to the electrode surface, which may also translate into a variation in bicarbonate concentration near the surface. Indeed, numerical models26,27 demonstrate that the necessary consumption of protons local to the catalyst surface results in a spatial and temporal concentration gradient in bicarbonate, however, these studies neglected to examine its effects on the rate of catalysts. To determine if the formation of a bicarbonate concentration gradient significantly convolutes the measured reaction order in bicarbonate we employed a stochastic method for kinetic simulations37–39 (computational details and input parameters in the SI and Table S3). We modeled the differences in reaction rate between a bicarbonate-mediated CPET (B.1. in Table 1) and bicarbonate-independent ET (A.1. in Table 1) mechanism as a function of the bulk [HCO3−]. This represents an advance relative to prior models that assume ET26 or do not explicitly delineate a RLS27–30. This model also incorporates the following key elements: (1) designation of bicarbonate as the explicit proton donor in contrast to prior models that use H2O26–30 and (2) inclusion of the slow hydration kinetics of CO2 (k3) and k2 in Fig. 1) in contrast to prior models26–30 that assume fast equilibration of CO2 and bicarbonate. This model assumes a boundary layer thickness of 1 μm. The model includes any convective or migratory components, and thus, the calculated gradients are expected to be greater than those existing at a planar electrode in a stirred electrolyte or on a rotating disk electrode18 and significantly smaller than those existing within a higher surface area, nanostructured, or highly porous electrode11,12. On highly nano/meso structured electrodes, the current may no longer be subject to purely activation control across the entire surface, impeding the accurate determination of intrinsic reaction orders and potentially explaining discrepancies10,40 in the literature.

Using this model, we probed the expected bicarbonate concentration gradients for CO2RR proceeding via rate-limiting ET (A.1. in Table 1) or bicarbonate-mediated CPET (B.1. in Table 1). Fig. 3 displays the calculated spatio-temporal bicarbonate concentration gradient for CO2RR occurring in 0.1 M NaHCO3 via CPET (a) or ET (b) pathways. Importantly, we observe maximum HCO3− depletion of −2 mM within 1 μm of the electrode surface for both the ET and CPET pathways. In 1.0 M NaHCO3 (Fig. S6), we find the same ~2 mM depletion for the ET pathway, but a ~20 mM depletion for the CPET case, reflective of higher jCO (see below). These trends indicate that the percent HCO3− depletion remains constant at ~2% for CPET, whereas the absolute depletion, ~2 mM, remains constant for ET. Thus, irrespective of the mechanism, local depletion effects negligibly impact the reaction order data collected between 30 and 300 mM, Fig. 2a, and provide additional confidence in assigning a p value of 0 in bicarbonate for Au-catalyzed CO2RR.

While [HCO3−] is changing minimally at the electrode surface, the consumption of protons in the overall reaction, combined with the sluggish CO2 hydration kinetics, leads to a substantial buildup in CO2− for CPET and ET pathways (Fig. S7). Using the Henderson-Hasselbalch equation, we calculate that this buildup in [CO2−] serves to raise the pH of the medium near the electrode surface to
-8.7 and 8.1-8.6 for 0.1 and 1.0 M bicarbonate electrolytes, respectively. Thus, although a higher [HCO₃⁻] leads to an elevated bulk pH at constant P_{CO₂} the local pH trends in the opposite direction due to the higher buffering capacity regardless of the mechanism of catalysis. Thus, the zero order [HCO₃⁻] dependence observed in Fig. 2a also implies a zero order dependence in pH for CO₂RR.

The stochastic model also provides a direct estimate of $j_{CO}$ for both CPET and ET pathways. Modeling of the bicarbonate-mediated CPET sequence shows an increase in initial $j_{CO}$ from ~1.3 to ~13 mA cm⁻² as the bulk concentration of bicarbonate increases from 0.1 to 1.0 M. The ~30% decay in current density for the CPET sequence in 1.0 M bicarbonate is attributed to ~30% depletion CO₂ at the electrode surface at higher $j_{CO}$ (Fig. S8). In contrast, the ET sequence shows no dependence on bicarbonate concentration, in line with the experimental data (Fig. 2a). Together, the simulations highlight how the rate of CO production catalysis is insensitive to changes in the bicarbonate concentration — bulk or interfacial — if the RLS of the catalysis only involves ET.

By comparing the experimental and simulated data with Tables 1, S1, and S2, we are able to elucidate the role of bicarbonate during Au-catalyzed CO₂RR. We measure a p value of 0 in bicarbonate and also infer a p value of 0 in pH. These results, combined with the first order dependence in CO₂ and the absence of a measurable H/D KIE, 18 argue against mechanisms involving hydronium, water, or bicarbonate as a proton donor in the RLS (Tables 1, S1-S2). This analysis leaves step A.1/D.1, electroosorption of CO₂, as the most viable RLS. Literature reports 8,16,17 and our previous studies 18 suggest a Tafel slope of >120 mV/dec over the potential range examined here, lending further support to mechanisms A and D as the most probable, with step A.1/D.1 as rate-limiting with a $\beta \sim 0.5$. Sequences A and D only differ by the pathway for addition of H/D equivalents to adsorbed CO₂ beyond the RLS and are therefore kinetically indistinguishable. Together, the data suggest that bicarbonate is not explicitly involved in the RLS of CO evolution on polycrystalline Au surfaces, and instead, acts as a viable proton donor past the RLS and a sluggish buffer that maintains the bulk but not local pH. While the explicit mechanistic role of bicarbonate for other catalyst surfaces remains an open question, this insight helps explain why inhibited diffusion in mesoporous electrodes, which would further deplete bicarbonate and raise pH, does not lead to a significant suppression in the rate of CO production. 23,35 The inability of bicarbonate to act as general acid motivates the development of designer electrolytes capable of promoting CO₂ activation at electrode surfaces via low-barrier CPET pathways.

ASSOCIATED CONTENT

Supporting Information
Experimental and computational details, derivations, cyclic voltammograms, additional simulation results. The Supporting Information is available free of charge on the ACS Publications website.

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REFERENCES

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