Kinetic Analysis on the Role of Bicarbonate in Carbon Dioxide Electreduction at Immobilized Cobalt Phthalocyanine

Joy S. Zeng, Nathan Corbin, Kindle Williams, and Karthish Manthiram*

1. INTRODUCTION

In electrocatalysis, it can be a challenging task to elucidate reaction mechanisms and develop structure–property relationships amid the complex interplay between catalyst, reacting species, solvent, ions, and electrostatic potential gradient. For carbon dioxide electroreduction (CO2RR) to carbon monoxide (CO) at immobilized cobalt phthalocyanine (CoPc) in aqueous electrolytes has been widely debated. In this work, we investigated the mechanism of CO2RR to CO on CoPc via experimental reaction kinetics coupled with model fitting. Unexpectedly, reactant order dependences and Tafel slopes deviate from commonly expected values and change depending on the testing conditions. For example, (1) the effect of bicarbonate deviates from power law kinetics and transitions from inhibitory to promotional with increasingly reductive potential, and (2) the CO2 order dependence deviates from unity at more-reductive potentials.

We propose a kinetic model, chosen from more than 15 candidate models, that is able to quantitatively fit all of the experimental data. The model invokes (1) catalyst poisoning via bicarbonate electro sorption, (2) mixed control between concerted proton–electron transfer (CPET) and sequential electron transfer-proton transfer (ET-PT), and (3) both water and bicarbonate as kinetically relevant proton donors. The proposed model also predicts that the relative importance of the above factors changes depending on the reaction conditions, highlighting the potential downfalls of broadly applying reaction mechanisms that were inferred from kinetic data collected in a narrow range of testing conditions. This study emphasizes the importance of cohesively using kinetic data collected over a wide range of operating conditions to test and formulate kinetic models of electrocatalytic reactions.

transfer is accompanied by a proton transfer in a concerted proton–electron transfer (CPET) mechanism or if the proton transfer occurs separately in a sequential proton–electron transfer (SPET) mechanism is unclear.

Reaction orders with respect to pH or bicarbonate concentration could be used to distinguish between SPET and CPET pathways. The only experimental kinetic study reporting a bicarbonate order dependence on CoPc for CO2RR was interpreted at constant voltage versus the reversible hydrogen electrode (RHE),9 whereas it should have been interpreted at constant voltage versus a pH-independent reference such as the standard hydrogen electrode (SHE).4,15 Kinetic studies on CoPc-like immobilized cobalt tetrapyrroles such as cobalt tetraphenyl porphyrin,16 cobalt tetraaminophenyl porphyrin,17 and iron–nitrogen–carbon catalysts18 have generally suggested that bicarbonate concentration or pH do not affect reaction rate, although studies on perfluorinated CoPc19 and cobalt...
protoporphyrin IX have suggested that the rate is pH dependent. Spectroscopic studies using in situ X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) and in situ Fourier-transform infrared spectroscopy (FTIR) have suggested that the CoPc-COOH intermediate forms and is observable during electrolysis but do not directly provide evidence for whether the intermediate forms from a CPET or SPET mechanism. Additionally, computational studies on CoPc-tetrapyroles have reported conflicting conclusions—some studies on cobalt porphine suggested the SPET mechanism is thermodynamically favored, whereas another study on the same catalyst suggested that both SPET and CPET mechanisms are possible and that the preference is pH-dependent. Notably, the above experimental and computational studies may not be comparable because they studied distinct, though similar, catalysts. Nevertheless, largely missing from these debates is a cohesive and comprehensive set of experimental kinetic data on CoPc to support or refute the various proposed mechanistic hypotheses.

Common strategies for studying electrocatalytic reaction mechanisms include collecting Tafel slopes and reaction orders, which are used to infer how many electrons and which reactants participate in reactions during or before the RDS. In simple kinetic limits, Tafel-slope and reaction-order analyses can be straightforwardly interpreted when reaction orders are integer values or the Tafel slope is of the form $\frac{60}{n+x/2}$ (where $n$ is an integer, $x$ is 0 or 1, and the transfer coefficient is assumed to be 1/2). However, in more complex limits of kinetic control, Tafel slopes or reaction orders may deviate from these easily interpretable values or change depending on reaction conditions. For example, it has been shown that Tafel slopes can take on almost any value when the coverages of adsorbed species deviate from the limits of 0 or 1. Typically in these more complex cases, any measured deviations from values associated with simple kinetic limits are only explained qualitatively. However, using the complex kinetic data to specifically and quantitatively test more nuanced mechanistic hypotheses could enhance the development and interpretation of structure-property relationships.

In thermal catalysis, it is more common to evaluate detailed mechanistic hypotheses by fitting multiparameter kinetic models to large sets of kinetic data. Such an approach has been used, for example, to study propylene oxidation and acetone conversion. In these contexts, it is well-accepted that macroscopically observed rates usually correspond to the complex interplay of multiple elementary reactions. In electrocatalysis, this complex interplay should also reasonably exist, but, save some exceptions, it is usually not quantitatively modeled and compared to experimental kinetic data.

In this work, we present a kinetic study on the mechanism of CO$_2$ reduction to CO on CoPc with kinetic data collected over a wide range of experimental conditions. Unexpectedly, we observe order dependences and Tafel slopes that deviate from commonly expected values and change depending on the testing conditions. To explain these trends, we propose a kinetic model, which was selected from a wide range of possible mechanistic models, that quantitatively fits all of the experimental data. We show that this model predicts the dominant kinetic mechanism changes depending on reaction conditions, highlighting the danger of broadly applying interpretations of kinetic data collected in a narrow set of testing conditions. This study provides some foundational framework for both understanding catalysis at atomically precise active sites and understanding the complex role of the electrolyte in electrocatalytic systems.

2. MATERIALS AND METHODS

2.1. Catalyst Preparation and Characterization. Catalyst electrodes were prepared following a previously reported procedure. Briefly, the catalyst, cobalt(II) phthalocyanine (Strem Chemicals), along with a conductive binder, Nafion (20 wt% dispersion, Fuel Cell Store), were dissolved in N,N-dimethylformamide (Anhydrous, 99.8%, Sigma-Aldrich) to form a catalyst ink. Carbon paper electrodes (Toray060, Fuel Cell Store) were first calcined at 800 °C in static air to make hydrophilic, oxidized carbon paper (OxCP). Catalyst inks were then drop-casted onto the OxCP electrodes. The electrodes were dried at 80 °C and used for kinetic tests within 24 h of preparation. Discussion about the use of Nafion in the electrode is included in SI Section 6.1.

Importantly, catalyst loading was kept below 5.8 x 10$^{-11}$ mol/cm$^2$. At this low loading, all deposited CoPc molecules were assumed to be active, and the turnover frequency was calculated by normalizing reaction rate to the total number of active sites deposited. It has been previously shown that testing in limits of low catalyst loading is essential for mitigating convoluting factors such as catalyst aggregation or mass transport limitations. Mitigating such factors is essential for extracting information about intrinsic turnover frequencies of individual catalyst molecules from bulk electrolysis measurements.

2.2. Kinetic Measurements. Catalyst electrodes were tested in a 3-compartment cell in which CO$_2$ flowed through the electrode (presumed to be flooded with electrolyte) and exited through the working compartment. Platinum foil was used as the counter electrode, leak-free Ag/AgCl (Innovative instruments) as the reference, and Nafion membrane the separator. Products were analyzed every 5 min via an online gas chromatograph (GC) (SRI instruments), and reported data points are averages over values collected at 10, 15, and 20 min marks, during which the GC-sampled headspace composition was expected to reflect steady-state conditions. All data were collected with 85% automatic resistance compensation.

Measurements were performed varying the following experimental settings: sodium bicarbonate (NaHCO$_3$) concentration, potential, and CO$_2$ partial pressure ($P_{CO_2}$). When varying [NaHCO$_3$], the total salt concentration was kept constant with sodium perchlorate (NaClO$_4$ > 98%, Sigma-Aldrich) as the balance. Keeping constant ionic strength helps keep the size of the electric double layer (EDL) and activities of ions roughly constant when changing electrolyte composition. Notably, because the thermodynamic activity of the gaseous reactant, CO$_2$, is set by the gaseous pressure in the headspace, keeping constant electrolyte ionic strength is not a necessary prerequisite for maintaining constant thermodynamic activity of CO$_2$. When $P_{CO_2}$ was varied, the total flow rate was kept constant, and nitrogen gas was used as the diluent. To measure the kinetic isotope effect (KIE), electrolytes were prepared by dissolving sodium carbonate (Na$_2$CO$_3$, 99.999%, Sigma-Aldrich) and NaClO$_4$ in deuterium oxide (D$_2$O, 99.9%, Sigma-Aldrich). Additional details about all experimental procedures can be found in SI Section 1.

For the most rigorous kinetic interpretation, any order dependence is reported at constant V vs the standard hydrogen electrode, a pH-independent reference point, because only then is it correct to directly interpret the slope of log(rate) vs...
log(reactant concentration) as the order of the reaction with respect to the varied reactant. This has been discussed in various places in the literature.4,15

2.3. Modeling and Parameter Estimation Techniques.

Modeling and parameter estimation were performed using the Athena Visual Studio (v14.2, W. E. Stewart and M. Caracotsios) statistical software package.34 Parameter estimation was performed via Bayesian estimation using the natural logarithm of rate as the single response variable. Using the logarithm of rate in the objective function implies an assumption of constant relative error in rate within all conditions tested.34 This assumption is consistent with the observation that residuals of the best fit model, calculated using logarithm of rate, appear normally distributed (vide infra). Lack-of-fit analysis was performed via an F-test, which is used to test the hypothesis that model and data came from the same distribution and that residuals between the model and data behave as one would expect for randomly distributed noise.34,35 The output of the F-test is an F-ratio, which represents model error divided by experimental error. The F-ratio can then be compared to an F-distribution, which is used to determine the probability of observing a higher F-ratio. This probability is denoted as α in this work, and larger α values indicate better goodness-of-fit. Finally, reported uncertainty intervals correspond to 95% highest posterior density intervals. Further details on model fitting can be found in SI Section 5.1.

3. RESULTS

3.1. Kinetic Measurements. The rate of CO₂RR to CO was measured at different NaHCO₃ concentrations, partial pressures of CO₂, and applied cathodic potentials. Highlighted below are the major observed trends, which are shown in Figure 1. It should be noted that, for clarity, Figure 1 shows only a representative subset of the kinetic data. A comprehensive table of data at all conditions tested can be found in the Supporting Information excel file.

When varying the concentration of NaHCO₃ at constant ionic strength and constant potential vs SHE, we observed non-power law behavior for the bicarbonate order dependence that shifted from an inhibitory effect of bicarbonate at less-reductive potentials to a promotional effect at more-reductive potentials (Figure 1a). Due to the equilibrium of CO₂ and water to make carbonic acid (H₂CO₃), the as-prepared concentration of NaHCO₃ is not exactly equal to the equilibrium concentration of bicarbonate (HCO₃⁻) anions at conditions of CO₂ saturation. Therefore, the x-axis variable in Figure 1a is the calculated equilibrium value, [HCO₃⁻]calc (details in SI Section 2). The lowest [HCO₃⁻]calc value of ≈1 × 10⁻⁴ M corresponds to no added NaHCO₃ (1 M NaClO₄). In this text, concentration of sodium bicarbonate will refer to the prepared concentration, and the calculated equilibrium value will be specifically denoted as [HCO₃⁻]calc.

Tafel behavior was found to vary depending on concentration of NaHCO₃ (Figure 1b). In the linear range, here taken to be less reductive than −1 V vs SHE, Tafel slopes decreased with increasing bicarbonate concentration (160 mV/dec in 0 M, 141 mV/dec in 0.1 M, and 86 mV/dec in 1 M NaHCO₃). Tafel slopes also generally increased with increasingly reductive potentials. Increasing Tafel slopes often indicate the onset of transport limitations, but we will later exclude this hypothesis.

The CO₂ order dependence was found to deviate from an expected value of 1 at more-reductive potentials (Figure 1c). This observation is consistent with a set of previously reported but unexplained CO₂ order dependencies on CoPc.9 As
evidence that the off-unity CO2 order dependence is not just due to measurement error, we also observed similarly depressed slopes at other NaHCO3 concentrations (Figure S13). Graphs explicitly showing linear regressions that gave the experimental slopes reported in Figure 1b,c are provided in Figures S11 and S12.

It is worth noting that in Figures 1a,c, because of the equilibrium between CO2 and carbonic acid, the pH also changes when [HCO3−]calc and PCO2 are varied. These bulk pH changes were accounted for in thermodynamically equilibrated steps during the kinetic modeling (Section 4.1.1) but turn out to not be physically significant in the final proposed mechanism. Please see SI Section 2.2 for an extended discussion.

Finally, kinetic-isotope-effect (KIE) measurements revealed that a proton likely participates in the RDS (Figure 1d). A KIE between 2 and 3 was measured in all of the representative experimental conditions tested. This value is consistent with KIE values that have previously been reported, by both experiment and theory, for CPET reactions. Although this KIE suggests that a proton participates in the RDS, it provides no information as to whether the source of the proton is hydronium, water, or bicarbonate.

3.2. Selectivity against HER and Stability. In this analysis, rate toward CO (and not the selectivity toward CO) was the considered dependent variable. Hydrogen evolution (HER) did also occur and was generally found to increase with more-reductive potentials (Figure S9). The selectivity toward CO generally had a wide range (from less than 50% to around 100%), and we expected that this was due to background HER and bicarbonate. We assumed that hydronium (H3O+) and bicarbonate were the more likely species to participate in relevant chemistry at the cathode.41 and (3) the interfacial concentrations of HCO3− and H2CO3 should be very current-sensitive, but we find that TOFCO does not have a clear dependence on total current (Figure S8).

The effect of the carbonate (CO32−) anion was also not considered. The concentrations of HCO3− and CO32− are practically difficult to independently manipulate, making effects that might be distinct to one ion or the other difficult to deconvolute. Because [CO32−] is orders of magnitude lower than [HCO3−] and because carbonate carries a greater negative charge, bicarbonate was considered to be the more likely species to participate in relevant chemistry at the cathode.

Finally, the oxidation state of the cobalt catalyst is not explicitly considered in this work. Though an interesting mechanistic detail and topic of debate,15 it is one that is not ascertainable via the kinetic analysis in this work because it is not relevant to the level of physical detail being modeled.

4.1.1. General Physical Assumptions. Equilibrium bulk electrolyte concentrations were used in the models. Although in CO2RR, it is well-known that interfacial conditions can deviate significantly from bulk conditions,3,39,40 we expected that the overall current densities observed in this kinetic study were low enough to reasonably neglect effects arising from mass transport limitations of species participating in the reaction. To evidence our assumption that mass transport limitations should not be at play, we looked at turnover frequency to CO, normalized by total deposited catalyst (TOFCO), as a function of loading. At the most reductive potential, which has the highest rates, we generally see, across several conditions, that there is no clear trend between TOFCO and loading, which suggests mass transport limitations should not be at play (Figure S8). If the reaction was mass transport limited, then we would expect TOFCO to decrease with loading, because total rate at the electrode would scale sublinearly with (and at the diffusion limited current, be invariant to) catalyst loading. One-dimensional coupled diffusion-reaction models, assuming either a planar electrode or a hemispherical catalyst, also suggest that for species considered kinetically relevant in our model, there is no significant deviation between bulk and interface concentrations. A more detailed discussion of these transport analyses can be found in SI Section 3.

Kinetically relevant proton donors were assumed to be water and bicarbonate. We assumed that hydronium (H3O+) and carbonic acid (H2CO3) were not kinetically relevant proton donors because (1) CO2RR is typically performed in near-neutral pH conditions, where [H3O+] and [H2CO3] are orders of magnitude lower than [HCO3−] or [H2O]; (2) there is literature precedent for favoring kinetically relevant proton donors other than hydronium during CO2RR due to alkalinity near the cathode;41 and (3) the interfacial concentrations of H3O+ and H2CO3 should be very current-sensitive, but we find that TOFCO does not have a clear dependence on total current (Figure S8).

The effect of the carbonate (CO32−) anion was also not considered. The concentrations of HCO3− and CO32− are practically difficult to independently manipulate, making effects that might be distinct to one ion or the other difficult to deconvolute. Because [CO32−] is orders of magnitude lower than [HCO3−] and because carbonate carries a greater negative charge, bicarbonate was considered to be the more likely species to participate in relevant chemistry at the cathode.

Finally, the oxidation state of the cobalt catalyst is not explicitly considered in this work. Though an interesting mechanistic detail and topic of debate,15 it is one that is not ascertainable via the kinetic analysis in this work because it is not relevant to the level of physical detail being modeled.

4.1.2. Enumeration of Possible Kinetically Relevant Steps. General literature precedent suggests that the resting state of the CoPc catalyst is unoccupied CoPc (species [1] in Figure 2a).18,21,23–25 From the resting state, the CoPc-COOH intermediate (species [2]) is likely formed from the transfer of CO2, a proton, and an electron.21,22 The possible routes we considered for achieving species [2] are illustrated in Figure 2a. They include a CPET mechanism (R1), and SPET mechanisms that involve electron transfer (ET) to CO2 followed by proton transfer (PT) (R2 followed by R3), or PT followed by ET (R4 followed by R5). Full reactions are written out in Table 1. A CPET step involving proton and electron transfer to form an adsorbed hydride was not considered because of the literature precedent suggesting that adsorbed hydride species on metal
tetrapyrroles typically lead to formate, rather than CO, production.42 We allowed for the possibility that any of the above paths from species [1] to [2] could occur and that any elementary step along those paths could be rate-determining. From here on, we will use the terminology “Rn” (for n = 1 to 5) to mean that the reaction proceeds along the path that Rn is a part of and that Rn is the RDS along that path. For example, a mechanism labeled R3 means that the mechanism consists of an ET step followed by a rate-determining PT step.

Any kinetic steps after the ones described above were not considered as possible rate-determining steps because high experimentally measured Tafel slopes indicated that the RDS should occur early in the catalytic cycle. Measured Tafel slopes were generally around 120 mV/dec, which suggested that the RDS was an initial ET or CPET step. We therefore only considered steps involving the first electron transfer and immediate subsequent chemical steps, but any further steps in the catalytic cycle including and beyond the second electron transfer would have, in the limit of no coverage effects, corresponded to 40 mV/dec (or lower) Tafel slopes and were therefore excluded. Explicit consideration and rejection of some possibilities are listed separately. The nine parameters used in the fitting parameters are associated with this mechanism.

Table 1. List of Elementary Reactions Considered

<table>
<thead>
<tr>
<th>label</th>
<th>full reaction</th>
<th>kinetic constants [unit]</th>
<th>thermodynamic constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (HCO3)</td>
<td>( \theta_1 + \text{CO}_2 + \text{HCO}<em>3 + e^- \rightleftharpoons \theta</em>{\text{COOH}} + \text{CO}_3^2^- )</td>
<td>( k_{\text{LHCO}<em>3}, \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1}; \beta</em>{\text{LHCO}_3} )</td>
<td>( K_1 \text{[atm]}^{-1} )</td>
</tr>
<tr>
<td>R1 (H2O)</td>
<td>( \theta_2 + \text{CO}_2 + \text{H}<em>2\text{O} + e^- \rightleftharpoons \theta</em>{\text{COOH}} + \text{OH}^- )</td>
<td>( k_{\text{LH}<em>2\text{O}}, \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1}; \beta</em>{\text{LH}_2\text{O}} )</td>
<td>( K_{\text{LH}_2\text{O}} \text{[mol/L]} )</td>
</tr>
<tr>
<td>R2</td>
<td>( \theta_2 + \text{CO}<em>2 + e^- \rightleftharpoons \theta</em>{\text{COOH}} )</td>
<td>( k_{\text{LCO}<em>2}, \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1}; \beta</em>{\text{LCO}_2} )</td>
<td>( K_{\text{LCO}_2} \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1} )</td>
</tr>
<tr>
<td>R3 (HCO3)</td>
<td>( \theta_{\text{CO}_2} + \text{HCO}<em>3 \rightleftharpoons \theta</em>{\text{COOH}} + \text{CO}_2^2^- )</td>
<td>( k_{\text{LHCO}<em>3}, \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1}; \beta</em>{\text{LHCO}_3} )</td>
<td>( K_{\text{LHCO}_3} \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1} )</td>
</tr>
<tr>
<td>R3 (H2O)</td>
<td>( \theta_{\text{CO}_2} + \text{H}<em>2\text{O} \rightleftharpoons \theta</em>{\text{COOH}} + \text{OH}^- )</td>
<td>( k_{\text{LH}<em>2\text{O}}, \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1}; \beta</em>{\text{LH}_2\text{O}} )</td>
<td>( K_{\text{LH}_2\text{O}} \text{[mol/L]} )</td>
</tr>
<tr>
<td>R4 (HCO3)</td>
<td>( \theta_4 + \text{HCO}_3 \rightleftharpoons \theta_4 + \text{CO}_2^2^- )</td>
<td>( k_{\text{LCO}<em>2}, \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1}; \beta</em>{\text{LCO}_2} )</td>
<td>( K_{\text{LCO}_2} \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1} )</td>
</tr>
<tr>
<td>R4 (H2O)</td>
<td>( \theta_4 + \text{H}_2\text{O} \rightleftharpoons \theta_4 + \text{OH}^- )</td>
<td>( k_{\text{LH}<em>2\text{O}}, \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1}; \beta</em>{\text{LH}_2\text{O}} )</td>
<td>( K_{\text{LH}_2\text{O}} \text{[mol/L]} )</td>
</tr>
<tr>
<td>R5</td>
<td>( \theta_5 + \text{CO}<em>2 + e^- \rightleftharpoons \theta</em>{\text{COOH}} )</td>
<td>( k_{\text{LCO}<em>2}, \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1}; \beta</em>{\text{LCO}_2} )</td>
<td>( K_{\text{LCO}_2} \text{[mol/L]}^{-1}\text{atm}^{-1}\text{s}^{-1} )</td>
</tr>
<tr>
<td>P1</td>
<td>( \theta_5 + \text{HCO}<em>3 \rightleftharpoons \theta</em>{\text{HCO}_3} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

“Associated kinetic constants (if the reaction was assumed to be an RDS) and thermodynamic constants (if the reaction was assumed to be equilibrated before an RDS) are also given. For R1, R3, and R4, proton transfer is assumed to occur from either HCO3 or H2O, and both possibilities are listed separately. The nine parameters used in the final proposed mechanism are in bold.

The turnover frequency (TOF) corresponding to each candidate RDS was expressed using Butler–Volmer kinetics:

\[
\text{TOF}_j = k_\theta e^{-\theta_j \phi / RT} \prod_{i \neq \text{react}} C_i^{\nu_i}
\]

where constant terms in the equation are defined as follows: \( x \) is the number of electron transfers that occur during the RDS (either 1 or 0), \( R \) is the ideal gas constant, \( T \) is the temperature in Kelvin, \( F \) is Faraday’s constant, \( \nu_i \) enumerates all of the reactants that occur in the forward reaction of the RDS, and \( \phi \) is the applied cathodic potential, and \( \{C_i \} \) are the stoichiometric coefficients of those species \( i \). Fitted parameters are defined as follows: \( k \) is the rate constant and \( \beta \) is the transfer coefficient of the RDS. Typically the transfer coefficient is assumed to be around 0.5, but in our general model formulation, \( \beta \) was allowed to vary between 0 and 1. Independent variables are the following: \( \phi \) is the applied cathodic potential, and \( \{C_i \} \) are the concentrations of the reactants. The term \( \theta \) corresponds to the fraction of CoPc catalyst sites occupied by a kth species and is the site at which the RDS proceeds. \( \theta \) incorporates additional concentration and potential dependences and is expressed using the definition of equilibrium:

\[
\theta_k = K_k \theta_{\text{LHCO}_3 \text{H}_2\text{O}} e^{\phi / RT} \prod_{i \neq \text{react}} C_i^{\nu_i}
\]

where \( K_k \) is the equilibrium constant, \( x \) is the number of electrons transferred to form \( \theta_k \) from \( \theta_{\text{LHCO}_3 \text{H}_2\text{O}} \) and \( \nu \) enumerates all of the reactants and products in the equilibrium, and \( \nu \) are the
stoichiometric coefficients of those species $m$ (positive for products, negative for reactants). The term $\theta_e$ corresponds to the fraction of unoccupied CoPc catalyst sites and is analytically determined from a site balance:

$$\theta_e = \frac{1}{1 + \sum \frac{\alpha_i}{\gamma_i}}$$

(3)

If multiple RDS possibilities were allowed to occur in parallel (for example, considering multiple proton donors for a single $R_n$ or, allowing multiple $R_n$ to occur in parallel), the total rate was expressed as the sum of the individual contributions:

$$\text{TOE}_{\text{total}} = \sum_j \text{TOE}_j$$

(4)

If two steps in series were both considered rate determining, a site balance was performed by assuming a steady-state concentration of the intermediate connecting the two kinetically relevant steps\(^{43}\) (SI Section 4.1).

4.1.3. Catalyst Poisoning Possibility. In addition to considering various possible rate-determining steps, we also allowed the possibility for bicarbonate to adsorb to and poison the catalyst (Figure 2b). Other electrolyte ions such as chloride\(^{44,45}\) phosphate\(^4\) and bulky cations\(^{46}\) have been implicated in having site-blocking effects on heterogeneous CO\(_2\)RR catalysts. We hypothesized that such poisoning could explain the inhibitory effect of bicarbonate that was observed at less-reductive potentials. In addition, because bicarbonate is a negatively charged anion and reductively polarizing an electrode to more negative potentials makes the electrode more negatively charged, it was also physically consistent that the apparent inhibitory effect of bicarbonate was attenuated at more-reductive potentials. Therefore, this poisoning mechanism, which we will label as P1, added $\theta_{\text{HCO}_3}$ to the set of $\theta_i$ in the site balance described in eq 3:

$$\theta_{\text{HCO}_3} = \theta_K \text{[HCO}_3^-]\text{e}^{\text{FF}/\text{RT}}$$

(5)

where $\gamma$ is the electrosorption valency of the bicarbonate anion and, in the limit of no charge transfer between adsorbed ion and electrode, is often interpreted to represent how far the charge on the adsorbed anion lies from the electrode divided by the characteristic length scale of the potential drop in the electric double layer. A $\gamma$ value closer to 1 indicates that the adsorbed anion’s negative charge resides at the electrode surface, whereas a $\gamma$ value closer to 0 indicates that the adsorbed anion’s negative charge lies outside of the double layer.\(^{37,46}\) Exclusion of other anions as poisoning species is discussed in SI Section 4.5, and discussion on the best-fit value of $\gamma$ can be found in Section 4.3.1.

4.1.4. Systematic Model Exploration. We enumerated all combinations of the RDS options shown in Figure 2a and the bicarbonate poisoning option in Figure 2b to generate a list of candidate kinetic models. Fully written reactions for these steps are given in Table 1. We generally considered up to two distinct RDSs as kinetically relevant (considered in either series or parallel, depending on whether or not they resided along the same reaction pathway). The assumption of rate-determining or kinetically relevant steps was taken to mean that any prior steps were in thermodynamic equilibrium, and any subsequent steps were rapid, implying no coverage effects from steps subsequent to the RDSs. These assumptions also implied that the energetic landscape of the catalytic cycle did not contain any large energy differences between intermediates other than in the kinetically relevant steps.\(^{39}\)

Parameters for the enumerated models were fit to experimental data, and the optimum parameter fits were used to evaluate candidate kinetic models. Rejected models had low goodness-of-fit statistics ($\alpha$ value) and also did not capture one or more of the qualitative order-dependence trends described above. The $\alpha$ value is an output of the F-test, which assesses the likelihood that the deviation of model from data is due to random error. Generally, $\alpha$ values below commonly cited cutoff values such as 0.05 or 0.01 indicate a model should be rejected.\(^{34,35}\) A subset of the considered RDS combinations is shown in Table 2. The models that are not explicitly listed in Table 2 had $\alpha$ values of 0 (all enumerated models can be found in Sections 4.3 to 4.5 of the SI).

### Table 2. Partial Enumeration of Candidate Models\(^a\)

<table>
<thead>
<tr>
<th>mechanism</th>
<th>total no. of parameters</th>
<th>$\alpha$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1: $R_1 + R_2 + P_1$</td>
<td>8</td>
<td>0.001</td>
</tr>
<tr>
<td>M2: $R_1 + R_3 + P_1$</td>
<td>9</td>
<td>0.109</td>
</tr>
<tr>
<td>M3: $R_1 + R_4 + P_1$</td>
<td>8</td>
<td>0.001</td>
</tr>
<tr>
<td>M4: $R_1 + R_5 + P_1$</td>
<td>9</td>
<td>0.001</td>
</tr>
<tr>
<td>M5: $R_2 + R_5 + P_1$</td>
<td>7</td>
<td>0.000</td>
</tr>
<tr>
<td>M6: $R_1 + P_1$</td>
<td>6</td>
<td>0.001</td>
</tr>
<tr>
<td>M7: $R_1 + R_3 + R_5$</td>
<td>10</td>
<td>0.000</td>
</tr>
<tr>
<td>M8: $R_1 + R_2 + R_3 + P_1$</td>
<td>11</td>
<td>0.109$^b$</td>
</tr>
</tbody>
</table>

$^a$Higher $\alpha$ values indicate better goodness of fit. $^b$Best-fit parameter values made the model equivalent to M2.

4.2. Proposed Mechanism for CO\(_2\)RR to CO on CoPc.

4.2.1. Model Description. The proposed mechanism (Model M2 in Table 2) includes mixed kinetic control between a CPET mechanism and an SPET mechanism (Figure 2c). The SPET mechanism consists of a facile ET step followed by a rate-determining PT step and can therefore be more specifically described as an ET-PT step. For both the CPET and ET-PT, both water and bicarbonate are proton donors. Additionally, the mechanism invokes catalyst poisoning via bicarbonate adsorption. TOF from the model is expressed as follows (precise expressions for each term can be found in Section 4.1.2 of the SI):

$$\text{TOF} = \frac{r_{\text{HCO}_3} + r_{\text{H}_2\text{O}} + r_{\text{H}_2\text{O}^+} + r_{\text{H}_2\text{O}}}{1 + \frac{\theta_{\text{HCO}_3}}{\theta_e} + \frac{\theta_{\text{H}_2\text{O}^+}}{\theta_e}}$$

(6)

where in total, there are nine fitting parameters: four kinetic rate constants, two CPET transfer coefficients, two equilibrium constants, and the bicarbonate electrosorption valency.
distribution of random error that is a prerequisite condition to the validity of a goodness-of-fit test such as the F-test.

4.2.3. Rejected Models. The following discussion of rejected models serves to illustrate that the kinetic steps invoked in model M2 were all necessary to describe the experimental data and that models which had similar complexity but invoked different kinetic steps were not able to fit the data. We find it necessary to include such a discussion because often, adding complexity to a model improves model fit simply by virtue of having more fitting parameters. From the discussion below, we would like to argue that the better fit of model M2 to the kinetic data was due to the inclusion of relevant chemistry and not just a general artifact of including more parameters.

The importance of bicarbonate poisoning is illustrated by the lack of fit of model M7 in Table 2. Even when a complex mixed control between three RDS steps is invoked, model M7 cannot capture the inhibitory effect of bicarbonate that is observed at less-reductive potentials (Figure 3a). The importance of allowing a CPET and an ET-PT step to occur in parallel is illustrated by the lack of fit of model M6 in Table 2. Without a parallel ET-PT pathway, model M7 is unable to capture the off-unity CO2 order dependences that were observed at more-reductive potentials (Figure 3b).

We also considered a model that allowed R1, R2, and R3 to all be kinetically relevant steps (M8 in Table 2), essentially adding extra parameters to relax the assumption that the electron transfer (R2) in the ET-PT pathway was rapid. The best-fit parameters from that model still converged to M2, predicting that the forward and reverse reactions of the electron transfer step (R2) were at least 2 orders of magnitude faster than the forward reaction of the proton transfer step (R3).

The lack of fit of all of the other excluded models enumerated in Table 2 and Supporting Information suggests that the chemistry specific to M2 was important for capturing the experimental observations. Of so many different enumerated model mechanisms, all with a similar number of fitting parameters, model M2 had, by far, the highest goodness-of-fit statistic and was the only model that could qualitatively capture the observed experimental trends. On the basis of these results, we propose model M2 to describe the complex interplay of anions and proton donors in CO2RR to CO on CoPc.

4.3. Physical Interpretation of the Kinetic Model.

4.3.1. Interpretation of Parameter Values. The best-fit parameter values, expressed with respect to the representation in which they were fit, are listed in Table 3. It is only meaningful to compare values of rate constants that correspond to reactions with the same potential dependence. This is due to the arbitrary referencing of potential that was used in this model (see SI Section 4.2 for details). Changing this arbitrary reference will change the relative magnitudes of rate constants that correspond to steps with different potential dependences. Therefore, we can only meaningfully compare rate constants in the protonation step, R3, and note that the rate constant for bicarbonate is larger than that for water ($k_{\text{HCO}_3^-} > k_{\text{H}_2\text{O}}$). This trend is qualitatively consistent with the physical intuition that bicarbonate is a stronger acid than water and should therefore donate protons more easily. Quantitatively, it might be surprising that the ratio between $k_{\text{HCO}_3^-}$ and $k_{\text{H}_2\text{O}}$ is lower than the ratio between $K_a$ values of bicarbonate and water. This discrepancy between thermodynamic driving force and kinetic rate for proton transfer is reported in similar contexts and may be due to local structure of solvation, ions, and electric fields near the electrode.

The transfer-coefficient values of the CPET step also have physical meaning. The transfer coefficient of the CPET with bicarbonate as the proton donor was, within error, approximately 0.5. In electrocatalysis, β is typically assumed to be 0.5. The transfer coefficient of the CPET with water as the proton donor was around 0.25, which is lower than this expected value. It has been postulated that transfer coefficients can deviate from 0.5 due to the structure of the proton donor or differences

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln(k_{\text{HCO}_3^-})$</td>
<td>3.4 ± 0.71</td>
<td>CPET (HCO3-) forward rate constant</td>
</tr>
<tr>
<td>$\ln(k_{\text{H}_2\text{O}})$</td>
<td>2.7 ± 0.15</td>
<td>CPET (H2O) forward rate constant</td>
</tr>
<tr>
<td>$\beta_{\text{HCO}_3^-}$</td>
<td>0.44 ± 0.20</td>
<td>CPET (HCO3-) transfer coefficient</td>
</tr>
<tr>
<td>$\beta_{\text{H}_2\text{O}}$</td>
<td>0.23 ± 0.05</td>
<td>CPET (H2O) transfer coefficient</td>
</tr>
<tr>
<td>$\ln(k_{\text{HCO}_3^-})$</td>
<td>6.1 ± 0.65</td>
<td>PT (HCO3-) forward rate constant</td>
</tr>
<tr>
<td>$\ln(k_{\text{H}_2\text{O}})$</td>
<td>3.5 ± 0.52</td>
<td>PT (H2O) forward rate constant</td>
</tr>
<tr>
<td>$\ln(K_a)$</td>
<td>−5.8 ± 0.59</td>
<td>ET equilibrium constant</td>
</tr>
<tr>
<td>$\ln(K_{\text{HCO}_3^-})$</td>
<td>2.6 ± 0.43</td>
<td>bicarbonate poisoning equilibrium constant</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.16 ± 0.12</td>
<td>bicarbonate electrosorption valency</td>
</tr>
</tbody>
</table>

* ± values indicate 95% highest posterior density intervals.
in charge distribution in the EDL.\textsuperscript{50} In this context, the physical reason for this low transfer coefficient may be a topic of further inquiry.

The electrosorption valency of bicarbonate adsorption was found to be around 0.2. This low value suggests that the negative charge of bicarbonate resides closer to the edge of the EDL than it does to the electrode surface. This value of 0.2 is conceivable given that the size of bicarbonate and the EDL are of similar magnitudes. The unsolvated, thermochemical radius of the bicarbonate anion is 156 pm,\textsuperscript{52} and the width of the EDL in 1 M salt is around 300 pm.\textsuperscript{26} In a carbonic anhydrase enzyme, the distance between the oxygens of a bound bicarbonate ion and the enzyme’s cobalt center was found to be around 250 pm.\textsuperscript{53} Additionally, it is conceivable that adsorbed bicarbonate could be polarized by the EDL such that most of its negative charge resides on the side that is farthest away from the electrode surface. However, given uncertainty about the actual bond distance between bicarbonate and CoPc, and general uncertainty about the molecular arrangement of ions, charge, and solvent in the EDL, a more specific geometric interpretation of this electrosorption valency value is difficult.

4.3.2. Model-Predicted Limits of Kinetic Relevance. The proposed kinetic model allows for occupation of CoPc by both adsorbed HCO$_3^-$ and CO$_2$, mixed control between CPET and ET-PT, and two kinetically relevant proton donors. The relative importance of these various effects are discussed below.

With respect to site occupation, the fraction of CoPc sites that are occupied by HCO$_3^-$ increases with [HCO$_3^-$] and decreases as applied potential becomes more reductive (Figure 4a). A more-reductive potential reduces HCO$_3^-$ occupation due to electrostatic repulsion between bicarbonate and a more negatively charged electrode. The fraction of CoPc sites that are occupied by CO$_2$ radical anion generally increases at more-reductive potentials (Figure 4b) because the formation of the CO$_2$ radical anion involves a reductive electron transfer. Higher CO$_2$ partial pressure also favors CoPc occupation by the CO$_2$ radical anion (Figure S19).

With respect to dominant reaction kinetics, the reaction shifts from CPET-dominant to ET-PT-dominant as the applied potential becomes more reductive (Figure 4c). This is because formation of the CO$_2$ radical anion, which is a step along the ET-PT pathway, has a stronger potential dependence (“60 mV/dec”) than the CPET step (“~120 mV/dec”). Interestingly, a shift from CPET to ET-PT at more-reductive potentials has also been proposed as a reaction mechanism for CO$_2$RR to CO on silver.\textsuperscript{54}

With respect to proton donor, bicarbonate is dominant at higher [HCO$_3^-$] and more-reductive potentials (Figure 4d). The kinetic relevance of HCO$_3^-$ should naturally be linked to its concentration, and the potential dependence can be explained as follows: at more-reductive potentials when ET-PT is dominant, HCO$_3^-$ is the dominant proton donor simply because $k_{HCO_3^-} > k_{H_2O}$. At less-reductive potentials when CPET is dominant, the importance of HCO$_3^-$ as a proton donor increases with more-reductive potentials because $\beta_{HCO_3^-} > \beta_{H_2O}$, which means that the rate of CPET with HCO$_3^-$ is more potential-sensitive.

The discussions above were considered at constant CO$_2$ partial pressure of 1 atm. Similar graphs at constant [HCO$_3^-$] and varying $P_{CO_2}$ can be found in the SI (Section 7). The only term with interesting CO$_2$ sensitivity was the occupation of
CoPc-COO\(^{-}\), which, as noted earlier, increased as \(P_{\text{CO}_2}\) increased.

4.3.3. Model-Based Explanation of Kinetic Data. From the physical trends discussed above, it is possible to explain the experimental trends shown in Figure 1. First, the bicarbonate order dependence at less-reductive potentials is negative because CoPc- HCO\(^{-}\) occupation is significant and HCO\(^{-}\) is not yet a significant proton donor. Therefore, the net effect of adding more bicarbonate is to inhibit rate. At more-reductive potentials, the poisoning effect of HCO\(^{-}\) becomes attenuated, and the importance of HCO\(^{-}\) as a proton donor increases. Therefore, at more-reductive potentials, the net effect of adding more HCO\(^{-}\) is to increase rate. To further support this hypothesis, we also measured bicarbonate order dependence in the presence of 0.5 M, pH 7 phosphate buffer (Figure S17). Because H\(_2\)PO\(_4\) has a \(pK_a\) of 7.2 whereas HCO\(^{-}\) has a \(pK_a\) of 10.33, when the two ions are present at similar concentrations, H\(_2\)PO\(_4\) should be the preferential proton donor. We did observe that at more-reductive potentials, in the presence of phosphate buffer, the apparent positive bicarbonate order dependence was attenuated.

Second, in the linear, low-overpotential regime, the Tafel slopes collected at high [HCO\(^{-}\)] were smaller than those collected at low [HCO\(^{-}\)]. The reason for this is 2-fold. First, in the low-overpotential regime, CPET is dominant. CPET with HCO\(^{-}\) as the proton donor is more dominant at higher [HCO\(^{-}\)] and has a lower Tafel slope than CPET with H\(_2\)O as the proton donor because \(\beta_{\text{HCO}_3^-} > \beta_{\text{H}_2\text{O}}\). Additionally, at higher [HCO\(^{-}\)], bicarbonate poisoning is a more important phenomenon. As a result, applying a more-reductive potential in higher [HCO\(^{-}\)] has a stronger effect in both promoting the Faradic reaction step and reducing the amount of bicarbonate poisoning, and should therefore have a lower Tafel slope. In the high overpotential regime, when the reaction shifts toward an ET-PT mechanism, all of the Tafel slopes increase. This is somewhat counterintuitive because the ET-PT mechanism is generally associated with a lower Tafel slope than the CPET mechanism. However, in this model, the Tafel slope increases due to coverage effects of the \(\theta_{\text{CO}_2}\) species from the equilibrated ET step in the ET-PT.

The off-shy CO\(_2\) order dependence at more-reductive potentials can be understood by coverage effects from occupation of CoPc-COO\(^{-}\) sites at more-reductive potentials. Since the occupation of CoPc-COO\(^{-}\) is in the site balance in the denominator of the rate equation, higher occupation of CoPc-COO\(^{-}\) results in a lowered rate. Therefore, when increasing the CO\(_2\) partial pressure, the competing effects of increasing the amount of reactant for an RDS step but also increasing CoPc-COO\(^{-}\) occupation result in apparent CO\(_2\) order dependences that are less than 1.

4.4. Related Systems. Non power law, inhibitory, and potential-dependent effects of bicarbonate concentration were also observed with immobilized cobalt tetraphenyl porphyrin (CoTPP) (Figure S18), which suggests that the mechanistic hypotheses presented in this work may also be relevant to other tetrapyrrole or tetrapyrrole-like CO\(_2\)RR catalysts. The specific generalization of this hypothesis to other catalysts could be the topic of future investigation.

5. CONCLUSIONS

In this work, we investigated the mechanism of CO\(_2\)RR to CO on CoPc through fitting kinetic models to experimental data collected over a wide range of testing conditions. Particularly when order dependencies and Tafel slopes deviate from commonly interpreted values, this strategy of simultaneously fitting a wide range of the kinetic data allows one to cohesively and quantitatively develop detailed mechanistic hypotheses.

The proposed mechanism itself may contain some interesting implications. First, the somewhat unconventional, though not unreported,\(^{25,54}\) mixed control between CPET and ET-PT suggests that it may be generally relevant to consider mixed control between these two pathways when studying electro-chemical reaction mechanisms and that the dominant mechanism can actually change depending on the operating conditions. This is important because the conditions at which kinetic data are collected may be different from practically relevant operating conditions, where different reaction kinetics could be at play. For example, electrochemical kinetic data is usually collected at low overpotentials to achieve low currents that avoid convolution with mass transport,\(^{3,5}\) but practical systems should have higher currents and may operate at higher overpotentials to drive that current. From our work, we see that the mechanism may change depending on the operating voltage and that this “voltage gap”, which could be analogous to the “pressure gap” that is well-acknowledged in thermal catalysis,\(^{35}\) cannot necessarily be ignored. Kinetic insights obtained from one set of testing conditions may not be generally applicable to a wider range of operating conditions. This also illustrates the point that when making comparisons across different catalysts to understand some type of structure—property relationship, the testing conditions at which the catalyst comparisons are made may influence which underlying physical phenomena are most dominantly at play.

Additionally, this model makes a quantitative prediction about various kinetic roles of bicarbonate in the catalysis—as a proton donor and as a catalyst poisoning species. Such a kinetic hypothesis may be very relevant to another open question in CO\(_2\)RR electrocatalysis: the role of electrolyte anions.\(^{56–61}\) Understanding the role of anions in general or the role of the bicarbonate anion specifically (which will always be present in CO\(_2\)RR due to the equilibrium between CO\(_2\) and water) is a complicated prospect because of the multifaceted roles that anions such as bicarbonate can assume. For example, bicarbonate may be thought of as a proton donor, pH buffer, or a generally charged electrolyte species; all of these physical roles could have separate influences on reaction rate through perturbing kinetics, mass transport, and the electric double layer. In this work, we were able to circumvent some of this complexity by studying a well-defined catalyst active site and operating in conditions where mass transport limitations did not affect the reaction kinetics. By quantitatively and specifically analyzing the kinetic role of bicarbonate in CO\(_2\)RR at a well-known catalyst, this study may augment the foundational basis and analytical framework for future work that seeks to generally understand the role of electrolyte composition in complex electrocatalytic systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.9b05272.

Reagent information, experimental protocols, modeling and parameter fitting details, control experiments (PDF)
Compilation of all experimental data used for model fitting including experimental condition, rate, and calculated species concentrations (XLSX)

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Notes
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REFERENCES


