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Functional Role of Pyridinium during Aqueous Electrochemical Reduction of CO_2 on Pt(111)

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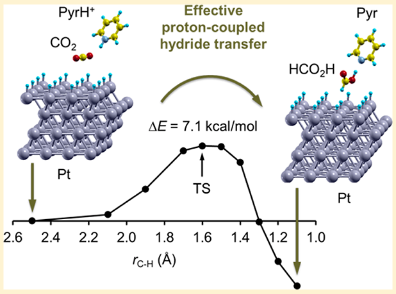
Supporting Information

ABSTRACT: Recent breakthroughs in electrochemical studies have reported aqueous CO_2 reduction to formic acid, formaldehyde, and methanol at low overpotentials (−0.58 V versus SCE), with a Pt working electrode in acidic pyridine (Pyr) solutions. We find that CO_2 is reduced by H atoms bound to the Pt surface that are transferred as hydrides to CO_2 in a proton-coupled hydride transfer (PCHT) mechanism activated by pyridinium ($PyrH^+$), $CO_2 + Pt{-}H + PyrH^+ + e^- \rightarrow Pyr + Pt + HCO_2H$. The surface-bound H atoms consumed by CO_2 reduction is replenished by the one-electron reduction of $PyrH^+$ through the proton-coupled electron transfer (PCET), $PyrH^+ + Pt + e^- \rightarrow Pyr + Pt{-}H$. Pyridinium is essential to establish a high concentration of Brønsted acid in contact with CO_2 and with the Pt surface, much higher than the concentration of free protons. These findings are particularly relevant to generate fuels with a carbon-neutral footprint.



SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis

The electrochemical reduction of carbon dioxide (CO_2)[1] is a process of great current interest because it could provide chemicals and fuels with a carbon-neutral footprint. Recently, Bocarsly and co-workers have achieved CO_2 reduction to formic acid, formaldehyde, and methanol at low overpotentials when using a Pt disk electrode in a 10 mM aqueous solution of pyridine (Pyr) at pH 5.3 (Figure 1).[2] The outstanding scientific challenge is to establish the reaction mechanism. However, a globally homogeneous process based on inner-sphere-type electron transfer from the pyridinium radical ($PyrH^•$) to the substrate (Scheme 1) has been suggested by Bocarsly and co-workers.[2] The key step in their mechanism is the generation of the $PyrH^•$ intermediate by one-electron reduction of the

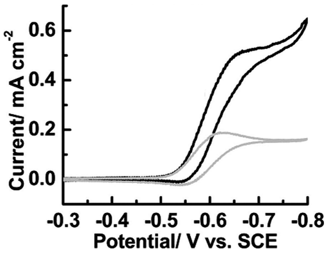
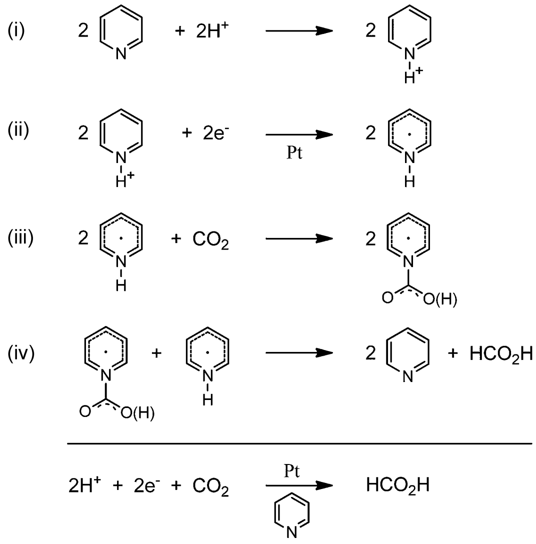


Figure 1. Cyclic voltammograms of $PyrH^+$ reduction in the presence of Ar (gray) and CO_2 (black) at pH = 5.3, obtained with a Pt disk electrode.[2] Figure reproduced from ref [2] with permission. Copyright American Chemical Society 2010.

Scheme 1. Previously Proposed CO_2 Reduction Mechanism Based on Formation of the Pyridinium Radical (ii), Followed by Inner-Sphere-Type Electron Transfer from the Pyridinium Radical to the Substrate (iii, iv)



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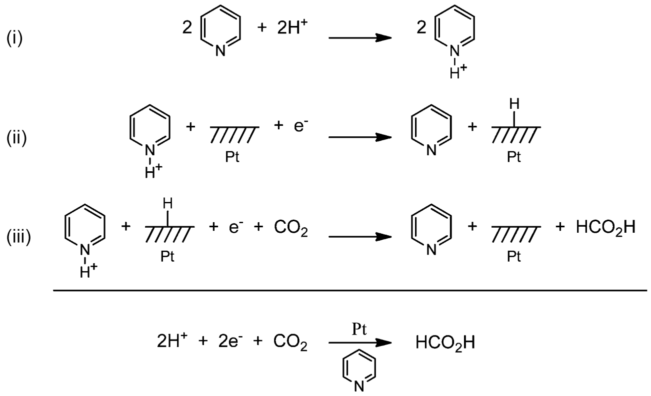
pyridinium cation ($PyrH^+$) (Scheme 1, ii). The $PyrH^\bullet$ species then reacts with CO_2 to generate a carbamate intermediate in the rate-determining step (Scheme 1, iii), a species recently probed by gas-phase vibrational spectroscopy.[3] Reduction of the carbamate by another $PyrH^\bullet$ produces formic acid (Scheme 1, iv), and further reductions involving the pyridinium radical form formaldehyde and then methanol.

A density functional theory (DFT) study has ruled out the possibility of $PyrH^\bullet$ generation in the homogeneous phase by reduction of $PyrH^+$ at overpotentials consistent with cyclic voltammetry (CV) measurements,[4] while a recent theoretical study has suggested the generation of $PyrH^\bullet$ on the surface.[5] Here, we explore whether the Pt surface can assist in the generation of the $PyrH^\bullet$ radical or if instead the reduction of $PyrH^+$ at low overpotentials generates other species that might be involved in the reduction of CO_2. A notable feature of the electrochemical process is the observation of a quasi-reversible one-electron cathodic wave of CV, corresponding to a reduction potential of about −600 mV versus SCE (Figure 1, black line). The sensitivity of the reaction to the nature of the working electrode shows significant activity for Pt but no catalytic current for glassy carbon electrodes at such low overpotentials.

In the present study, we focus on understanding aqueous CO_2 reduction to formic acid on the Pt(111) surface in the presence of pyridinium ions. Our free-energy analysis of reaction intermediates reveals a simple mechanism (Scheme 2). As shown below, an important step of Scheme 2 that bears an electrochemical signature consistent with the observed quasi-reversible cathodic wave is the pyridinium-facilitated formation of hydrogen atoms adsorbed on the Pt electrode surface (Scheme 2, ii). The generated hydrogen adsorbates are susceptible to electrophilic attack by CO_2 in the presence of $PyrH^+$ (Scheme 2, iii), and they are transferred as hydrides to the CO_2 substrate in an effective proton-coupled hydride transfer (PCHT) mechanism.

Scheme 2. Proposed Mechanism of Electrochemical Reduction of CO_2 on Pt(111), in an Aqueous Acidic Pyridine Solution, Based on Our DFT Calculations at the PBE Level of Theory



$PyrH^+$ functions as an electrocatalyst that establishes an effective concentration of Brønsted acid in contact with the Pt surface that is much higher than the concentration of protons in solution. Therefore, while hydrogen adsorbates could also result from reduction of free protons, the pyridinium reduction by PCET is predominant because the pyridinium concentration is about 1000 times the proton concentration under typical experimental conditions (e.g., 10 mM pyridine (Pyr) solutions at pH 5.3 have $[PyrH^+] = 4.26$ mM and $[H^+] = 5.0 \times 10^{-3}$ mM because the pK_a of $PyrH^+$ is 5.17). $PyrH^+$ also functions as the proton donor, with a concentration that is much higher than the concentration of protons in solution during the PCHT step, and activates CO_2 during the electrophilic attack by stabilizing the transition state through hydrogen bonding.[6]

Our free-energy analysis of the overall reaction mechanism, outlined in Scheme 2, is based on the gradient-corrected PBE level of theory[7] within the plane-wave-based pseudopotential scheme implemented in the Quantum ESPRESSO software package.[8] Ultrasoft pseudopotentials were employed for Pt, C, H, N, and O atoms with plane wave kinetic energy cut off values of 40 and 480 Ry for the wave functions and the charge densities, respectively. The Pt(111) surface was modeled by periodically repeating a 4 × 4 supercell (11.32 Å × 11.32 Å) in a four-layer slab in which the two bottom layers were fixed at the optimized bulk lattice constants. The Monkhorst−Pack type of *k*-point sampling with 2 × 2 × 1 grid points was used for periodic slab calculations. The bulk solvation effects were accounted for through the analysis of cluster models extracted from the optimized supercells with periodic boundary conditions, employing the SMD continuum solvation model[9] as implemented in Gaussian09[10] at the PBE level of theory (see the Supporting Information for more details). Redox potentials ($E^0 = -nF\Delta G^0$, with F as the Faraday constant and n as the number of electrons involved in the redox process) were obtained by computing the half-reaction free-energy change $\Delta G^0 = \Delta H - T\Delta S$, using the standard Born−Haber thermodynamic cycle as presented in a recent work.[11]

Direct calculations of the reduction potential of $PyrH^+$, forming hydrogen atoms adsorbed on the Pt electrode surface (Scheme 2, ii), are challenging. However, the overall free-energy change can be obtained by summing the three free-energy changes associated with the thermodynamic cycle of elementary steps (ii.1−ii.3), described in Scheme 3, including desorption of $PyrH^+$ from the surface (ii.1), two-electron reduction to form H_2 (ii.2), and dissociative adsorption of H_2 on the Pt surface. Our results, however, clearly show that the reaction (ii) proceeds *directly* as a one-electron reduction consistent with CV and *not* through the sequence of steps (ii.1−ii.3) involving nonspontaneous endothermic desorption (ii.1) and the two-electron reduction (ii-2).

Scheme 3. Computational Steps (ii.1−ii.3) Used to Obtain the Free-Energy Change Due to the Overall Reaction (ii) with $PyrH^+$ Reduced to Hydrogen Adsorbed on the Pt Surface

$$\begin{tikzcd}
\mathrm{PyrH^+}(ad) + \mathrm{Pt}(s) + e^- \arrow[r, "\text{(ii)}"] \arrow[d, "\text{(ii.1)}"'] & \mathrm{Pt\text{-}H}(s) + \mathrm{Pyr}(aq) \\
\mathrm{PyrH^+}(aq) + \mathrm{Pt}(s) + e^- \arrow[r, "\text{(ii.2)}"] & 1/2\ \mathrm{H_2}(g) + \mathrm{Pt}(s) + \mathrm{Pyr}(aq) \arrow[u, "\text{(ii.3)}"']
\end{tikzcd}$$

Free-energy calculations for the elementary steps (ii.1−ii.3) predict endothermic, nonspontaneous desorption of PyH^+ from Pt(111) (Scheme 3, ii.1) with $\Delta G^{desorp} = 9.9$ kcal mol^{-1} (see the Supporting Information for more details). The two-electron aqueous reduction of $PyrH^+$ to H_2 and Pyr (Scheme 3, ii.2) is predicted to require a potential $E^0[PyrH^+/H_2] = -0.59$ V versus SCE, while the dissociative adsorption of H_2 to the Pt(111) surface is spontaneous (Scheme 3, ii.3), with $\Delta G^{diss} =$

-6.9 kcal mol^{-1}. The sum of the three steps gives a total free-energy change for aqueous reduction of pyridinium to hydrogen on the Pt surface (Scheme 3, ii) at $E^0 = -0.72$ V versus SCE, in good agreement the quasi-reversible reduction observed by CV (Figure 1). These results suggest that the onset of the cathodic peak could be the result of direct reduction of $PyrH^+$ adsorbed on the Pt surface, through a one-electron process that leaves hydrogen atoms adsorbed on the Pt surface, as shown in Scheme 3, ii. In contrast, the reduction of $PyrH^+$ to $PyrH^\bullet$ in aqueous solution requires a much higher over-potential ($E^0[PyrH^+/ PyrH^\bullet] = -1.58$ V versus SCE) which, in agreement with Keith et al.,[3] is predicted to be 1.0 V more negative than the onset of the experimental cathodic wave (Figure 1).[11]

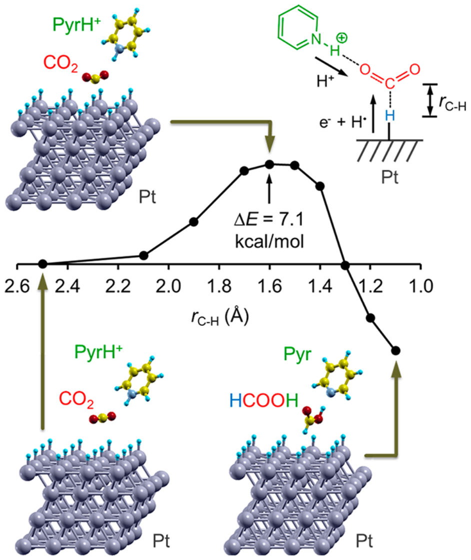


Figure 2. (Top) Reaction energy profile along the effective PCHT reaction in which CO_2, activated by $PyrH^+$, reacts with hydrogen on the Pt (111) surface, as shown in the inset (top right), calculated at the DFT PBE level of theory. Also shown are optimized structures obtained at the same level of theory with the (Pt)H−C(O_2) bond distance r_{C-H} constrained at 1.1, 1.6, and 2.5 Å.

The free-energy analysis also shows that the hydrogen adsorbates can reduce CO_2, as described in Scheme 2, iii, through an effective PCHT reaction at the Pt(111) surface. Figure 2 shows the PCHT energy profile along the electrophilic attack as CO_2 approaches the hydrogenated supercell in the model system $[Pt_{64}H_{16}CO_2PyrH]^0$. Each point along the reaction pathway corresponds to a geometry optimized at the PBE level of theory, subject to the constraint of fixed distance between the carbon atom of CO_2 and one of the hydrogen atoms initially adsorbed on the Pt(111) surface. These results show that CO_2 reduction could proceed with a modest energy barrier of ∼7 kcal mol^{-1} (at C−H ≈ 1.6 Å) by PCHT. Solvation corrections account for a 3 kcal mol^{-1} decrease in the reaction barrier, while the free-energy penalty due to the entropic cost of bringing $CO_{2(aq)}$ to the Pt surface is estimated to be 8.5 kcal mol^{-1} from thermodynamic data,[12] giving an overall free-energy barrier of ∼13 kcal mol^{-1}, in reasonable agreement with experimental predictions.[13] The resulting PCHT mechanism therefore involves an effective two-electron transfer, with a proton transfer from $PyrH^+$ and a concerted transfer of a hydrogen atom and an electron from the electrode surface. This PCHT avoids the formation of highly unstable intermediates such as the one-electron-reduced species $CO_2^{-\bullet}$, or $PyrH^\bullet$. The reaction, however, requires a hydrogenated electrode surface and the presence of the proton donor $PyrH^+$ at a sufficiently high concentration, as under typical experimental conditions where $[PyrH^+] \gg [H^+]$.

The PCHT mechanism suggested by our free-energy analysis is consistent with the observed kinetics of the reaction reported by Bocarsly and co-workers, showing that the rate is first-order in both CO_2 and $PyrH^+$.[13] The mechanism is also consistent with the sensitivity of the reaction to the nature of the electrode surface because only surfaces that could adsorb hydrogen atoms (i.e., reduced protons) are expected to show catalytic activity. Furthermore, the PCHT mechanism is consistent with the observed pH-independent redox potential and with the nonintuitive effect of pH on the reaction yield. While it might be thought that lowering the pH would enhance electrocatalytic activity by increasing the concentration of proton donors, in practice, lowering the pH enhances H_2 evolution as a competing reaction that lowers the yield of CO_2 reduction.

In summary, the reported analysis of aqueous CO_2 reduction to formic acid on Pt(111) surfaces in pyridine solutions suggests that the pyridinium cation undergoes a one-electron reduction, $PyrH^+ + Pt + e^- \rightarrow Pyr + Pt{-}H$, forming hydrogen atoms adsorbed on the Pt surface, at a pH-independent potential under the reported experimental conditions where $[PyrH^+] \gg [H^+]$. The hydrogen adsorbate is susceptible to electrophilic attack by CO_2, leading to a two-electron PCHT reaction, $CO_2 + Pt{-}H + PyrH^+ + e^- \rightarrow Pyr + Pt + HCO_2H$, that is first-order in both CO_2 and $PyrH^+$. $PyrH^+$ is essential to establish an effective concentration of Brønsted acid in contact with the Pt surface that is much higher than the concentration of protons in solution and to activate CO_2 during the PCHT. These findings should be particularly valuable for the design and development of new technologies that would generate fuels with a carbon-neutral footprint using aqueous solutions of organic electrocatalysts for CO_2 reduction at low over-potentials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting Information includes coordinates and thermodynamic data for the structural models reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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