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## Isotopic Probe Illuminates the Role of the Electrode Surface in Proton Coupled Hydride Transfer Electrochemical Reduction of Pyridinium on Pt(111)

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A recently proposed mechanism for electrochemical CO<sub>2</sub> reduction on Pt (111) catalyzed by aqueous acidic pyridine solutions suggests that the observed redox potential of ca. -600 mV vs. SCE is due to the one-electron reduction of pyridinium through proton coupled electron transfer (PCET) to form H atoms adsorbed on the Pt surface (H<sub>ads</sub>). The initial pyridinium reduction was probed isotopically via deuterium substitution. A combined experimental and theoretical analysis found equilibrium isotope effects (EIE) due to deuterium substitution at the acidic pyridinium site. A shift in the cathodic cyclic voltammetric half wave potential of -25 mV was observed, consistent with the theoretical prediction of -40 mV based on the recently proposed reaction mechanism where pyridinium is essential to establish a high concentration of Brønsted acid in contact with the substrate CO<sub>2</sub> and with the Pt surface. A prefeature in the cyclic voltammogram was examined under isotopic substitution and indicated an H<sub>ads</sub> intermediate in pyridinium reduction. Theoretical prediction and observation of an EIE supported the assignment of the cathodic wave to the proposed reduction of pyridinium through PCET forming H<sub>ads</sub> and eventually H<sub>2</sub> on the Pt surface.

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Efficient and quantitative reduction of carbon dioxide to interesting or useful chemicals is challenging and is under vigorous investigation.<sup>1-3</sup> Electrochemical reduction of carbon dioxide has the unique advantage of direct applied potential control over the energy of one of the reactants, the electron, however the overpotential required for reduction remains high at many electrochemical interfaces. This fact indicates that electrode surfaces as catalysts either do not significantly lower the activation barrier for CO<sub>2</sub> reduction or proceed through high energy intermediates. In order to provide lower energy pathways to CO<sub>2</sub> reduction and pursue mechanistic understanding, solution based catalysts have been employed.<sup>2,4,5</sup> Pyridinium (PyrH<sup>+</sup>) catalyzes the electrochemical reduction of CO<sub>2</sub> to methanol and formic acid at a platinum (Pt) electrode at low overpotentials (ca. -600 mV vs. SCE).<sup>6,7</sup> The mechanism of CO<sub>2</sub> reduction was proposed to initiate with the electrochemical reduction of PyrH<sup>+</sup>. Originally it was believed that this reduction proceeded through the ring π\* system generating a pyridinyl radical.<sup>6,7</sup> This radical was postulated to bind CO<sub>2</sub>, forming the active intermediate in the electron transfer to CO<sub>2</sub>.<sup>8</sup> Evidence for the proposed mechanism included digital simulation of the cyclic voltammetric scan rate dependence on a Pt electrode, an observed first order dependence of current on concentrations of both PyrH<sup>+</sup> and CO<sub>2</sub>, as well as density functional theory (DFT) calculations.<sup>6,8,9</sup> Reduction of CO<sub>2</sub> to methanol has also been observed photochemically in the presence of PyrH<sup>+</sup>, indicating that PyrH<sup>+</sup> reduction may be possible in homogeneous solution using a photocatalyst with suitably negative excited state redox potentials,<sup>10</sup> as had been indicated by quenching measurements.<sup>11</sup> Additionally, a vibrational spectrum indicative of carbamate formation has been observed in the gas phase upon reaction of CO<sub>2</sub><sup>•-</sup> with pyridine.<sup>12</sup> More recent work suggests that pyridinium reduction involves the acidic proton not the ring system.<sup>11</sup>

The assignment of the reduction at approximately -600 mV vs. SCE to the formation of pyridinyl radical was initially challenged by computational studies that indicated a significantly more negative reduction potential for PyrH<sup>+</sup> than that observed at a Pt

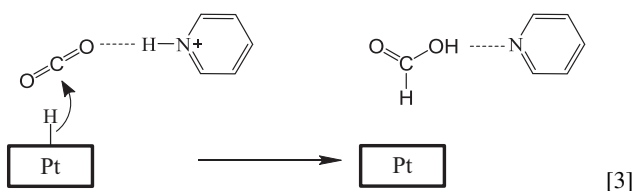
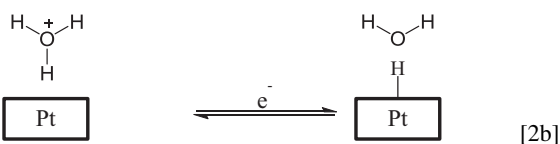
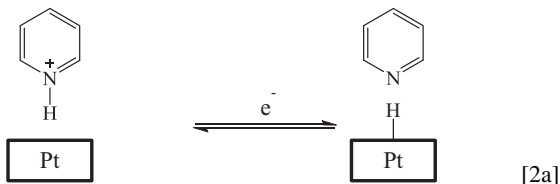
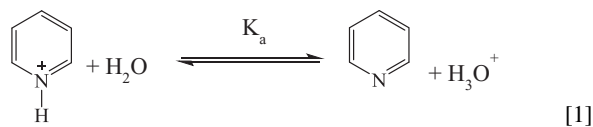
electrode.<sup>13,14</sup> In response to this discrepancy, several other mechanistic pathways were proposed for the initial reduction of PyrH<sup>+</sup> and subsequent reduction of CO<sub>2</sub>, including two electron reduction of PyrH<sup>+</sup> to dihydropyridine,<sup>14</sup> assisted deprotonation of pyridinyl via a hydrogen bound intermediate,<sup>15</sup> and specific adsorption of PyrH<sup>+</sup> or pyridinyl.<sup>13,15</sup> However these possible reaction mechanisms did not find experimental support when a Pt electrode was employed.<sup>11,16</sup> Pyridinium reduction has recently been explored at other electrode surfaces, including Ir and Au.<sup>17,18</sup> In the case of Au, specific adsorption of pyridinium is implicated, and for Ir the formation of pyridyl as a primary reduction product does not appear to be supported.

Another mechanism that has been proposed for the electrocatalytic reduction of CO<sub>2</sub> to methanol, in the presence of PyrH<sup>+</sup> on a Pt electrode, involves the initial generation of PyrH<sup>+</sup> through a pre-equilibrium between Pyr and PyrH<sup>+</sup> at pH = 5.2 (Eq. 1), followed by 1e<sup>-</sup> reduction of PyrH<sup>+</sup> on the Pt(111) surface to generate adsorbed hydrogen atoms (H<sub>ads</sub>) on the electrode (Eq. 2).<sup>19</sup> Finally, electrophilic attack of CO<sub>2</sub> on H<sub>ads</sub> causes a hydride ion transfer, which is facilitated by PyrH<sup>+</sup> acting as a proton donor (Eq. 3).<sup>19</sup> The net effect of the reaction sequence is a proton coupled hydride transfer (PCHT). There is an important subtlety in this reaction scheme. Namely, that an aqueous electrolyte composed of a weak acid provides two sources of protons: hydronium via Equation 2b and the weak acid itself (pyridinium in Equations 1 and 2a). If Equation 1 presents a rapid equilibrium, then in fact protons are delivered from only one source. That is both sides of Equation 1 provide protons and those protons are reduced at the electrode surface at a rate that is slow compared to the equilibration rate represented in this equation. Thus, there is a time averaged proton environment at the electrode interface, and at the point of reduction either acid source may be supplying the proton. As the rate of proton reduction increases with respect to the rate of hydrogen exchange, however, either Equation 2a or the direct reduction of H<sub>3</sub>O<sup>+</sup> Equation 2b can dominate the reaction. This issue is not only of interest in the case of pyridinium reduction that is evaluated here, but is of general interest with regard to weak acid reductions. Currently, reaction branching of this type is an open question for a number of electrochemical reactions that incorporate

\*Electrochemical Society Active Member.

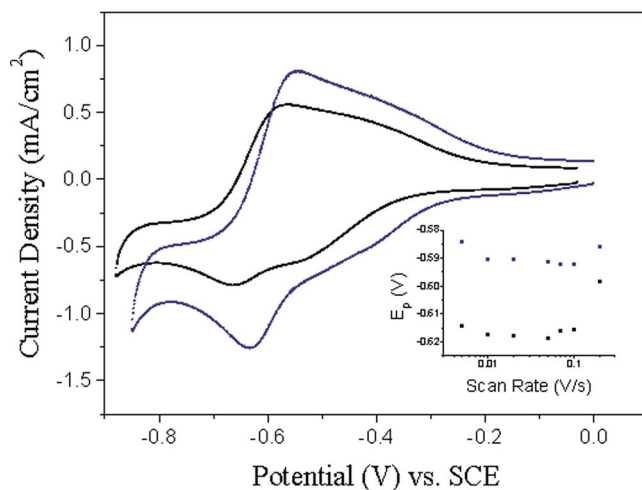
<sup>z</sup>E-mail: [bocarsly@princeton.edu](mailto:bocarsly@princeton.edu); [victor.batista@yale.edu](mailto:victor.batista@yale.edu)

proton reduction.



Platinum is unique in providing a catalytic surface for reduction reactions of protons. Additionally,  $\text{PyrH}^+$  and other weak acids have been found to reduce at more modest potentials at Pt cathodes than at other electrode materials. Reductive hydrogen atom adsorption from strong and weak acid solutions at Pt electrodes has been investigated and has been observed in steady state voltammetry at a microdisk electrode,<sup>20</sup> in sum frequency generation IR spectroscopy<sup>21</sup> and in surface enhanced Raman spectroscopy.<sup>22</sup> Specifically, under potential deposition (UPD) of a monolayer of strongly adsorbed hydrogen from  $\text{H}_3\text{O}^+$  is well established on Pt surfaces.<sup>23–28</sup> At the potentials under consideration in this work, an UPD hydrogen monolayer is expected to be present on (111) facets of the Pt electrode surface at three fold fcc sites.<sup>29,30</sup> At the  $\text{H}_2/\text{H}^+$  redox potential, a submonolayer of more weakly adsorbed hydrogen atoms (OPD H) is formed in an on top configuration, from which hydrogen evolution has been attributed.<sup>31</sup> In addition,  $\text{PyrH}^+$  reduction to  $\text{H}_{\text{ads}}$  on Pt and pyridine has been previously suggested in a study of dissociation of weak acids.<sup>32</sup> The proposed mechanism of  $\text{PyrH}^+$  reduction on Pt electrode surfaces has further support from an examination undertaken by the Bocarsly group of the dependence of weak acid standard redox potentials on  $\text{p}K_a$  for a series of acids reduced at a Pt electrode<sup>11</sup> which has recently been confirmed in a study of  $\text{PyrH}^+$  and weak acid proton reduction on Pt.<sup>16</sup>

Proton coupled electron transfer (PCET) mechanisms such as that proposed in Equation 2 are anticipated to exhibit isotope effects upon substitution of the acidic hydrogen by deuterium. Substitution by the heavier isotope is expected to affect the current in cyclic voltammetry via change in the diffusion coefficient upon deuteration. Deuteration also affects the reaction thermodynamics via change in the free energy of the acid dissociation equilibrium resulting from the changes in zero point energy (ZPE) and entropy of the deuterated versus protonated acid.<sup>33</sup> The change in zero point energy upon deuteration will be greater in bonds where the X-H or X-D bond is stronger. This greater stabilization favors deuterium equilibration into the more tightly bound state. An N-H bond is more tightly bound than a Pt-H bond, and thus in an N-H to Pt-H PCET, deuterium substitution would be expected to favor reactants, leading to a normal equilibrium isotope effect (EIE). In this study, the observed isotope effect combined with the theoretical analysis provide evidence of the breaking of the N-H bond during  $\text{PyrH}^+$  reduction, in agreement with the recently proposed mechanism for electrocatalytic reduction of  $\text{CO}_2$  via platinum hydride formation in the presence  $\text{PyrH}^+$ .



**Figure 1.** Cyclic voltammograms (CV) of pyridinium 10 mM aqueous solution (at pH or pD = 3.0) in  $\text{H}_2\text{O}$  (gray) and  $\text{D}_2\text{O}$  (black) taken at 100 mV/s, showing a shift in the half-wave potential for reduction upon deuteration. Inset is the half wave potentials plotted over log scan rate for  $\text{D}_2\text{O}$  (black) and  $\text{H}_2\text{O}$  (gray).

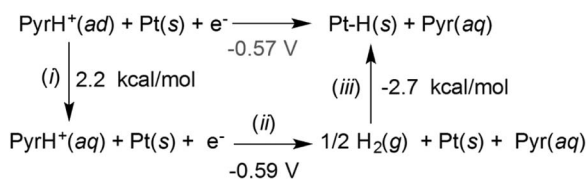
## Results and Discussion

Figure 1 shows that the reduction of  $\text{PyrH}^+$  at pH 3.0 in aqueous KCl solution produces a cyclic voltammogram wave with an invariant half-wave potential  $E_{1/2} = -0.590 \pm 0.002$  V vs. SCE, over scan rates of 5–200 mV/s. The scan rate range was chosen where the peak to peak separation was less than 100 mV, indicating no complications from a prefeature observed in acid reductions on Pt.<sup>11</sup> In Figure 1, an additional reduction process was observed at approximately  $-0.42$  V vs. SCE and was attributed to reduction of  $\text{H}_3\text{O}^+$  from water due to a proton concentration in the bulk of 1 mM at pH = 3.0. The reduction of protons derived from water and that derived from  $\text{PyrH}^+$  at a platinum cathode can be described as proton reduction to  $\text{H}_2$  where the formal potential for any acid,  $E_0^{\prime \text{HA}/\text{H}_2}$ , is simply that for proton reduction  $E_0^{\prime \text{H}_3\text{O}^+/\text{H}_2}$  modulated by the acid dissociation constant  $K_a$ , of HA Equation 4.<sup>11,32</sup>

$$E_0^{\prime \text{HA}/\text{H}_2} = E_0^{\prime \text{H}_3\text{O}^+/\text{H}_2} + \frac{RT}{F} \ln K_a \quad [4]$$

The formal potential is the thermodynamic standard potential modulated by experimental conditions such as ionic strength and solvent medium. As already noted, weak acids often dissociate before reduction. This process has been documented on platinum disk microelectrodes,<sup>34,35</sup> suggesting that proton reduction from hydronium is the likely process in either direct hydronium or  $\text{PyrH}^+$  reduction cases. Using the relationship in Equation 4 and approximating hydronium and  $\text{PyrH}^+$  reduction as reversible over the scan rates chosen so that the formal potential,  $E_0^{\prime \text{HA}/\text{H}_2} \cong E_{1/2}$ , the  $E_{1/2}$  values calculated for hydronium and  $\text{PyrH}^+$  protons are estimated to be  $-0.42$  V vs. SCE and  $-0.55$  V vs. SCE, close to that observed experimentally.

We performed density functional theory (DFT) calculations at PBE level of theory<sup>36</sup> (see supporting information for details) to compute the overall free energy change for the reduction of  $\text{PyrH}^+$  on Pt(111) surface, as obtained by summing the free energy changes of the three elementary steps in the thermodynamic cycle given in Scheme 1.<sup>19</sup> Scheme 1, ii represents the net reaction proposed to be occurring in the cyclic voltammetry under an Ar atmosphere, which is in good agreement with the observed reduction potential of  $-0.59$  V vs. SCE. It also is interesting to examine the calculated energies for formation of Pt-H, the proposed active intermediate. The reduction potential of adsorbed  $\text{PyrH}^+$  to form Pt-H on Pt(111) (Scheme 1) was calculated



**Scheme 1.** Thermodynamic cycle (i)–(iii) used to obtain the free energy change due to the overall reaction where  $\text{PyrH}^+$  is reduced to hydrogen adsorbed on the Pt surface.

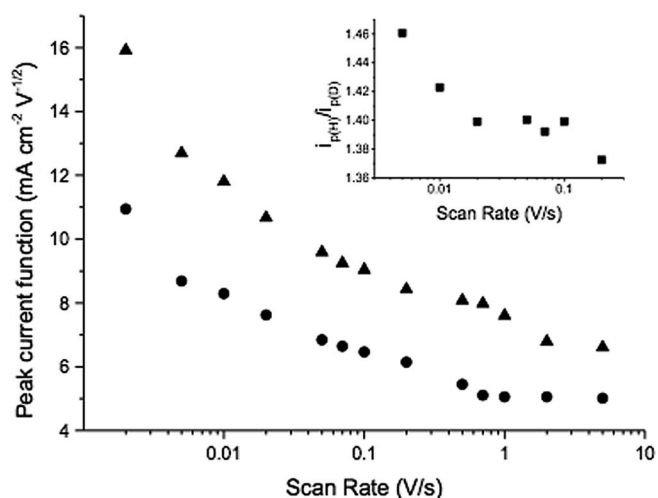
to be  $-0.57$  V vs. SCE which is also in good agreement with the reduction potential observed by cyclic voltammetry (CV) experiments.

Cyclic voltammetry and DFT calculations were performed to understand the effect of deuteration on the reduction of  $\text{PyrD}^+$  at Pt(111). In deuterated electrolyte, the half-wave potential for  $\text{PyrH}^+$  reduction was also invariant, but it was shifted to  $-0.614 \pm 0.005$  V vs. SCE, a change in  $\Delta E_{1/2} = -25$  mV relative to the non-deuterated electrolyte. Similar to the potential shift observed for acids of different strengths, the observed potential shift for  $\text{PyrH}^+$  vs.  $\text{PyrD}^+$  can be attributed to an increase in the free energy demand for deprotonation of  $\text{PyrH}^+$  of approximately  $+0.4$  pK<sub>a</sub> units under deuteration (Table I).<sup>37</sup> The effective change in pK<sub>a</sub> of acids upon deuteration was reported very soon after the discovery of deuterium.<sup>38–40</sup> Increases in pK<sub>a</sub> of approximately 0.5 units for deuterated vs. undeuterated acids were observed with weaker organic acids exhibiting greater shifts.<sup>41</sup> Simple substitution of the EIE on K<sub>a</sub> into Equation 4 indicates that a shift in 0.4 pK<sub>a</sub> units produces a change in redox potential of  $-23$  mV, close to the  $-25$  mV observed experimentally. Incorporation of  $E_0^{D_3O^+/D_2} = -0.013$  V into Equation 4 results in a final  $\Delta E_{1/2}^{\text{D-H}}$  calculated from experimental parameters for  $\text{PyrH}^+$  of  $-0.36$  V. Significantly, other weak acids exhibit similar equilibrium isotope shifts in cyclic voltammetry half wave potential with deuteration of the exchangeable position (Table I). A plot of cyclic voltammetric half wave potential vs. pK<sub>a(D)</sub> results in Equation 5.

$$E_{1/2} = -0.061 \times pK_{a(D)} - 0.26 \quad [5]$$

Similar to the empirical equation for protonated weak acids,<sup>11</sup> the rate of change in cyclic voltammetric potential with pK<sub>a</sub> was  $61 \pm 6$  mV, close to 59 mV as predicted by the Nernst equation, and the intercept was  $0.26 \pm 0.04$  V, close to the standard potential of  $\text{D}_3\text{O}^+/\text{D}_2$ . It is generally regarded that the mechanism for proton reduction at platinum electrodes involves a surface bound platinum hydride. Table I shows that weak acids of varying structure experience a similar shift in half-wave potential upon substitution of the acidic proton with a deuteron. An identical shift is observed between the  $\text{H}_3\text{O}^+$  and  $\text{D}_3\text{O}^+$  systems. Because the shift in half-wave potential is invariant with the structure of the molecule delivering the proton, it can be inferred that these reactions proceed by a similar mechanism. Thus, we invoke a surface  $\text{H}_{\text{ads}}$  intermediate for weak acid reduction at a platinum electrode.

In addition, a shift of  $-40$  mV was found for the reduction potential of  $\text{PyrD}^+$  relative to  $\text{PyrH}^+$  in process ii, corresponding to a free energy



**Figure 2.** Pyridinium reductive peak current function ( $i_p/v^{1/2}$ ) vs. scan rate for protonated solution (triangles) and deuterated solution (circles) at pH or pH\* = 3.0. The protonated peak current is uniformly greater than the deuterated current, with the ratio of peak currents shown in the inset.

change of  $0.9$  kcal mol<sup>-1</sup>, determined by changes in zero point energies and entropic contributions obtained via periodic DFT calculations. These computational results are consistent with the experimentally observed shift of the reduction potential of  $-25$  mV, supporting the assignment of the reductive wave to the  $1e^-$  reduction of  $\text{PyrH}^+$  to  $\text{H}_{\text{ads}}$  and ultimately  $\text{H}_2$  on the Pt(111) electrode surface.

To investigate if the shift in the reduction potential can be produced by changes in the chemical equilibrium of  $\text{PyrH}^+$  induced by deuteration of non-exchangeable positions, the reduction potential of  $\text{d}_5$ -pyridinium in water was measured by scan rate dependent cyclic voltammetry. A 10 mV shift of the potential of  $\text{PyrH}^+$  reduction was observed which is significantly smaller than the shift observed upon deuteration of  $\text{PyrH}^+$  at the exchangeable (nitrogen) position. Our observations are consistent with equilibrium isotope effects of similar magnitude determined electrochemically for naphthalene- $\text{h}_8/\text{d}_8$  and anthracene- $\text{h}_{10}/\text{d}_{10}$  in THF, with shifts of  $-13$  and  $-12$  mV respectively.<sup>43</sup> The greater isotope shift of  $\sim -25$  mV, observed for  $\text{h}_5$ - $\text{PyrD}^+$  in  $\text{D}_2\text{O}$ , is consistent with the participation of an exchangeable proton in the reduction half reaction and further rules out direct charge transfer to the ring  $\pi$ -system, which would lead to an isotopic shift of half size observed based on the results reported above.

Figure 2 shows the peak current density vs. scan rate for deuterated and protonated solutions at pH or pH\* = 3.0. Under these conditions,  $\text{PyrH}^+$  should be  $>99\%$  protonated/deuterated. Peak current in a cyclic voltammogram (Equation 6), when divided by the square root of the scan rate ( $i_p/v^{1/2}$ ) to yield the peak current function, gives a measure of the resulting reaction rate after removing the time dependence associated with diffusion of the reactant(s) to the electrode

**Table I.** Half wave potential for reduction of various weak acids at a Pt electrode in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  electrolytes from our cyclic voltammetry, literature pK<sub>a(H)</sub><sup>42</sup> and our calculated pK<sub>a(D)</sub> values (Supporting Information).<sup>37</sup> Errors for measured  $E_{1/2}$  values were taken as the 95% confidence interval from the mean  $E_{1/2}$  taken from 5–200 mV/s.

Acid	pK <sub>a(H)</sub>	pK <sub>a(D)</sub>	$\Delta pK_{a(D-H)}$	$E_{1/2 \text{ H}}$ (V vs. SCE)	$E_{1/2 \text{ D}}$ (V vs. SCE)	$\Delta E_{1/2 \text{ (D-H)}}$ Exp. (V)	$\Delta E_0^{\text{(D-H)}}$ (V) calc. from $\Delta pK_{a(D-H)}$ , $\Delta E_0^{\text{H}_3\text{O}^+/\text{H}_2}$ and Eq. 4
2,6-lutidinium	6.70	7.21	0.51	$-0.680 \pm 0.001$	$-0.702 \pm 0.001$	$-0.022 \pm 0.002$	-0.043
4-methyl pyridinium	5.99	6.45	0.46	$-0.629 \pm 0.002$	$-0.662 \pm 0.001$	$-0.032 \pm 0.003$	-0.040
Pyridinium	5.23	5.63	0.40	$-0.590 \pm 0.002$	$-0.614 \pm 0.005$	$-0.025 \pm 0.007$	-0.036
Acetic acid	4.756	5.12	0.36	$-0.554 \pm 0.003$	$-0.577 \pm 0.001$	$-0.023 \pm 0.004$	-0.034
Benzoic acid	4.204	4.52	0.32	$-0.511 \pm 0.001$	$-0.538 \pm 0.002$	$-0.023 \pm 0.003$	-0.032

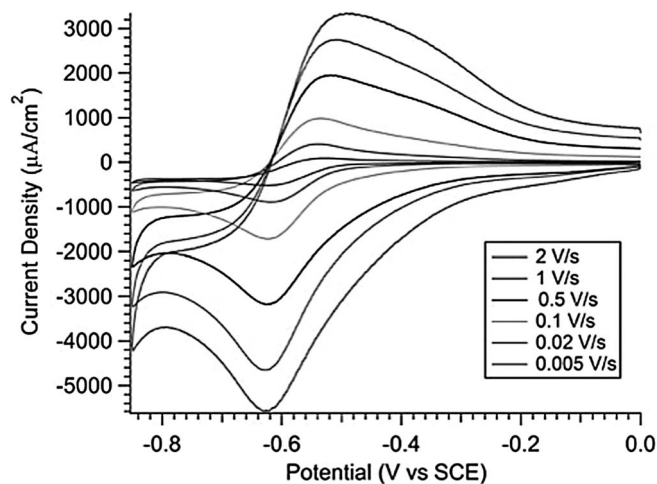
surface.<sup>44</sup>

$$i_p = 2.69 \times 10^5 n^{3/2} AC_O^* D^{1/2} \nu^{1/2} \quad [6]$$

The peak current function should be independent of the scan rate for a reversible electron transfer without coupled chemical steps according to Equation 6. However, as shown in Fig. 2, we observed that the peak current for both deuterated and protonated electrolytes increased at low scan rates, suggesting that there is a slow chemical step coupled to PyrH<sup>+</sup> reduction.<sup>44</sup>

The ratio  $i_{p(H)}/i_{p(D)}$  can reflect changes in the diffusion coefficient induced by deuteration. The diffusion coefficients for PyrD<sup>+</sup> and PyrH<sup>+</sup> were calculated from combined cyclic and rotating disk voltammetric studies (see supporting information). The diffusion coefficient for PyrH<sup>+</sup>,  $D_{\text{PyrH}^+}$ , in 0.5 M KCl has been reported to be  $2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  using this method.<sup>11</sup> The number of electrons transferred and calculated diffusion coefficient for PyrD<sup>+</sup> from combined cyclic voltammetric and rotating disk studies is  $n = 0.9 \pm 0.1$  and  $D_{\text{PyrD}^+} = 9.4 \times 10^{-6} \pm 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  respectively (Figure S1). This results in a value of 2.2 for  $D_{\text{PyrH}^+}/D_{\text{PyrD}^+}$ . Given that the rotating disk data confirms that  $n = 1$ , the ratio  $D_{\text{PyrH}^+}/D_{\text{PyrD}^+}$  can also be obtained from the ratio of the squares of the peak cyclic voltammetric currents observed for PyrH<sup>+</sup> vs. PyrD<sup>+</sup>. The necessary data is provided in Figure 2 and produces a value for  $D_{\text{PyrH}^+}/D_{\text{PyrD}^+}$  of  $2.1 \pm 0.1$  confirming the result of the RDE experiment. Similarly, diffusion coefficients for D<sub>3</sub>O<sup>+</sup> in D<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup> in H<sub>2</sub>O have been reported to be  $6.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $9.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , respectively at infinite dilution, leading to a ratio of  $D_{\text{H}^+}/D_{\text{D}^+} = 1.4$ .<sup>45,46</sup> In solutions of increasing ionic strength up to 0.5 M KCl solutions, the ratio of diffusion coefficients for  $D_{\text{H}^+}/D_{\text{D}^+}$  has been reported to be between 1.4 and 1.8.<sup>45,46</sup> The ratio of peak currents for proton and deuteron reduction at a platinum electrode,  $i_{\text{H}}/i_{\text{D}}$ , was measured and found to be 1.2 (Table S1). Squaring the current ratio leads to a projected diffusion coefficient ratio of 1.4 ( $\pm 0.1$ ) for  $D_{\text{H}^+}/D_{\text{D}^+}$ , the same as observed in the reported studies. Thus, both the pyridinium and hydronium data indicate that for H and D, peak current ratios can be explained by the change in diffusion coefficient upon deuteration. Overall the pyridinium related diffusion coefficients are smaller ( $\sim 20\%$ ) than the hydronium diffusion coefficients as expected for a process that is limited by simple diffusion versus proton hopping. The isotopic (H/D) ratios of hydronium diffusion coefficients (1.4) versus pyridinium diffusion coefficients (2.1) are statistically different at the 95% confidence level. This is consistent with pyridine acting as a “proton shuttle” that brings this species up to the electrode reaction zone. However, given that proton exchange between pyridine and water is expected to be rapid, no conclusions can be drawn about the nature of the protonic species undergoing the reduction associated with the cyclic voltammetric wave centered at  $-0.59 \text{ V vs. SCE}$ . However, it is interesting to note that the quantum mechanical analysis presented here, which assumes that the absorbing species undergoing reduction is pyridinium (not hydronium) produces a model that is consistent with the data presented here.

As already noted the existence of a surface adsorbed hydrogen intermediate is well documented in the reduction of hydronium (generated by a strong acid) by both electrochemical measurements and spectroelectrochemical observations. However, the explicit observation of a surface platinum hydride has not been well documented for weak acids at moderate pHs. However, we find a very distinctive feature in the cyclic voltammetric response of pyridinium at platinum electrodes that we directly correlate with the existence of a surface platinum hydride intermediate. As shown in Figure 3, at scan rates above  $\sim 200 \text{ mV/s}$  a distinctive prefeature exists leading to a distortion of the positive potential side of the pyridinium wave. At slow scan rates (up to  $100 \text{ mV/s}$ ), the voltammetry appears reversible. Analysis of this voltammetric feature is complicated by the extensive convolution of the prewave with the diffusive peak at slow to moderate scan rate. In order to deconvolute the distorted wave into the diffusive wave and this peak, a wave with reversible behavior was subtracted from the distorted wave. This was achieved by scaling a slow scan rate (where



**Figure 3.** Scan rate dependence of the cyclic voltammetric response of 10 mM pyridine, pH 5.1 at a platinum working electrode in aqueous KCl solution. At fast scan rates, the electrochemical behavior noticeably deviates from reversibility.

the electrochemical behavior appears to be reversible) by the constant factor  $\sqrt{\frac{\nu_{fast}}{\nu_{slow}}}$  to simulate the voltammetric response of the reversible behavior at the fast scan rates. This scaled slow scan rate data was subtracted from the distorted scan. In all cases,  $\nu_{slow}$  is the 20 mV/s scan, where there is no convective interference with the voltammetry as demonstrated by digital simulation of the cyclic voltammetry at that scan rate. Figure 4a shows an overlay of the residual current resulting from the data subtraction for the prefeature at 2000 mV/s under both H<sub>2</sub>O and D<sub>2</sub>O conditions. The subtracted prefeature undergoes the same shift as the diffusive wave upon deuteration; however, as shown in Figure 4b, it scales linearly with scan rate, as would be expected of an adsorbed species. A Nernstian adsorbate layer follows the equation<sup>47</sup>

$$i_p = \frac{n^2 F^2}{4RT} \nu A \Gamma_O^* \quad [7]$$

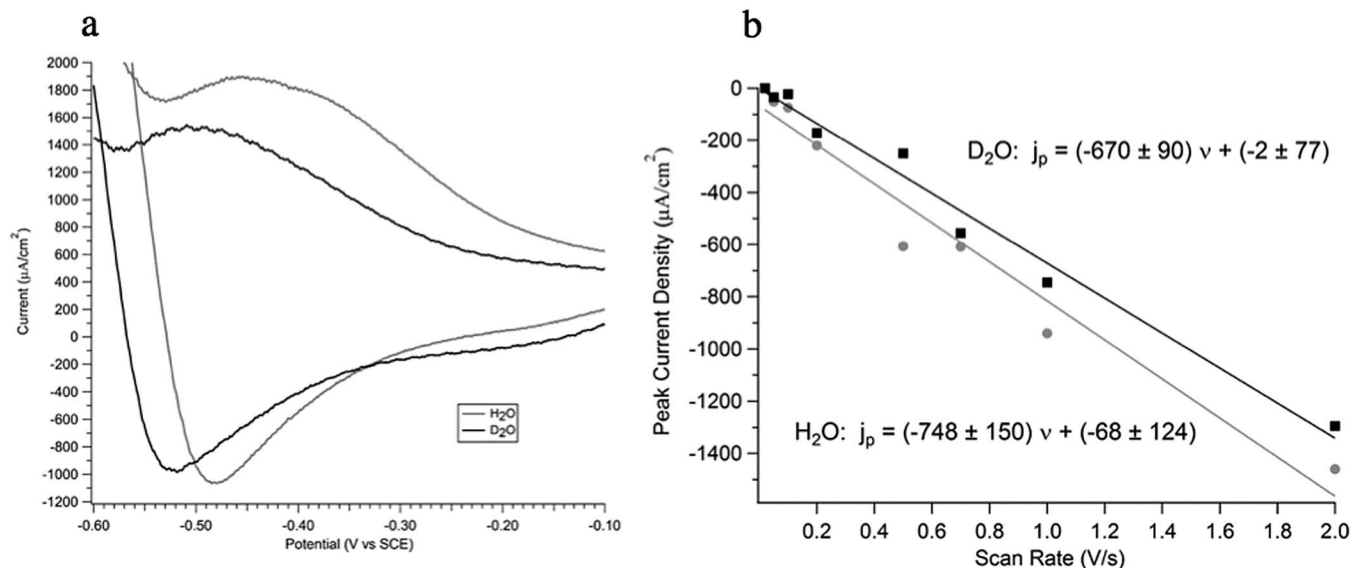
It is noted that for electrodes with the same surface area, the slope depends only on standard constants and the surface coverage  $\Gamma_O^*$ . Because the slopes of Figure 4b agree within a 95% confidence limit, it can be stated that the surface species in these cases have the same value of  $\Gamma_O^*$ , as would be expected for  $H_{ads}$  and  $D_{ads}$ .

In further support of the assertion that this voltammetric feature is the  $H_{ads}$  species, careful analysis of the thermodynamic data presented in Scheme 1 predicts that an  $H_{ads}$  should occur at  $-0.475 \text{ V vs. SCE}$ , the same as the experimentally observed potential for the prefeature, which occurs at  $-0.485 \text{ V vs. SCE}$  at 2000 mV/s, as shown in Figure 4a. Taking the reverse of path i, 2.2 kcal/mol can be converted to a potential scale via Faraday's constant to give 0.095 V. This can then be added to path iv, which is predicted to occur thermodynamically at  $-0.57 \text{ V}$ . The addition of these two values gives a potential of  $-0.475 \text{ V vs. SCE}$ , which coincides with the potential of the prefeature, lending support to the assignment of this feature as a  $H_{ads}$  intermediate.

This analysis of the system supports the presence of an  $H_{ads}$  intermediate in the proton reduction of weak acids at platinum electrodes. The fact that the purely thermodynamic data strongly supports this conclusion suggests that this reduction is not kinetically limited.

## Methods

**Computational methods.**— Density functional theory (DFT) calculations were carried out at the gradient-corrected PBE level of theory<sup>36</sup> within the plane-wave pseudopotential scheme as



**Figure 4.** a) adsorptive peak obtained via subtraction of scaled cyclic voltammograms from 2000 mV/s scan. b) linear response of peak reduction potential with scan rate.

implemented in the Quantum ESPRESSO<sup>48</sup> software package to model Pt(111) surface similar to our previous work.<sup>19</sup> Two significant differences from our prior work are that (i) the Pt(111) surface was modeled by a periodically repeating  $3 \times 3$  supercell ( $8.47 \text{ \AA} \times 8.47 \text{ \AA}$ ) in a four-layer slab where the two bottom layers were fixed at the optimized bulk lattice constants and (ii) as the Pt(111) surface is expected to have near 1 ML hydrogen ad-atom coverage at fcc sites at the experimental conditions, a surface coverage of  $8/9$  is chosen for the calculations. The Monkhorst-Pack type of  $\mathbf{k}$ -point sampling with a  $2 \times 2 \times 1$  grid was chosen for the slab calculations and the convergence in binding energies were further checked by employing denser  $\mathbf{k}$ -point grids of  $3 \times 3 \times 1$  and  $6 \times 6 \times 1$ . Select geometries for the cluster calculations were fully optimized at the PBE level of density functional theory<sup>36</sup> using the Stuttgart ECP60MWB contracted pseudopotential basis set<sup>49</sup> for Pt and the 6-31G(d) basis set<sup>50</sup> for all other atoms. The grid = ultrafine option (in Gaussian 09)<sup>51</sup> was chosen for integral evaluation and an automatically generated density-fitting basis set was used within the resolution-of-the-identity approximation for the evaluation of Coulomb integrals. Solvation effects associated with water as solvent were accounted for by using the SMD aqueous continuum solvation model.<sup>52</sup> The aqueous solvation contribution to the plane-wave-based periodic DFT optimized structures were calculated via generating model clusters with 14 Pt atoms and performing single point calculations at the PBE level of density functional theory using SDD basis set for Pt and the 6-311+G(2df, p) basis set for all other atoms while restricting the spin state of model structures to open-shell singlet or doublet states. The equilibrium isotope effect (EIE) associated with deuterium exchange of acidic hydrogen of  $\text{PyrH}^+$  is predicted via performing phonon calculations at the  $q = \Gamma$  point only to obtain the vibrational frequencies associated with the H ad-atom and  $\text{PyrH}^+$  on a Pt(111) fcc site. The vibrational frequencies are used to calculate the changes in ZPE and entropic contributions due to H/D exchange, which in turn are employed to predict the EIE. Further details on computational methods are available in the supporting information.

**Materials.**— Supporting electrolyte KCl (EMD, 99%) was dried in a vacuum oven at  $100^\circ\text{C}$  for at least 3 hours prior to experiment and mixed at 0.5 M concentration with either deionized water or D<sub>2</sub>O (Cambridge Isotope Labs, 99.9%). Pyridine (Sigma Aldrich, 99.8%), potassium acetate (Alfa Aesar, 99%), sodium benzoate (JT Baker), 2,6-lutidine (Sigma Aldrich, 98%) and 4-methylpyridine

(Sigma Aldrich, 98%) were used in 10 mM concentration at their  $\text{pH} = \text{pKa}$  or  $\text{pD} = \text{pKa(D)}$ , for a bulk protonated (deuterated) acid concentration of 5 mM or for examination of peak currents, at  $\text{pH} = \text{pH}^* = 3.0$ . Pyridine was distilled over calcium hydride. All solid analytes were dried in a vacuum oven at  $100^\circ\text{C}$  for at least 3 hours prior to use. 4-methylpyridine and 2,6-lutidine were used as received.

**Cyclic voltammetry.**— Cyclic voltammograms were recorded on either CHI 760 or CHI 1140 potentiostats with instrument error of less than 5 mV. Saturated calomel (SCE) reference half cells (Accumet), Pt mesh counter electrodes and Pt disk working electrodes (BASi,  $0.020 \text{ cm}^2$  area) were used in a standard 3 electrode configuration. The working electrode was cleaned between each scan rate by polishing with  $1 \mu\text{m}$  alumina particles (Fisher) on cloth pads. Glassware was dried in a  $100^\circ\text{C}$  oven for at least 30 minutes prior to use. Solutions were purged with Ar to exclude O<sub>2</sub>. The pH reading in D<sub>2</sub>O solution of a standard pH meter calibrated in pH 4, 7 and 10 H<sub>2</sub>O-based buffers (Fisher), termed  $\text{pH}^*$ , was adjusted to the pKa of the acid as measured in H<sub>2</sub>O (for pyridine, adjusted  $\text{pH}^* = \text{pKa(H)} = 5.2$ ) using 0.1 M DCl (Aldrich, 99.9%) in D<sub>2</sub>O. According to the formula in Krężel, for the acids in question this should result in a pD and pKa(D) values shifted by 0.4 pH units, (for pyridinium,  $\text{pD} = \text{pKa(D)} = 5.63$ ). For evaluation of the cyclic voltammetric peak current in pyridinium reduction, pH or  $\text{pH}^*$  of the solution was adjusted to 3.0, where 99% of the analyte is protonated. Scan rates of 5–2000 mV/s were recorded.

**Rotating disk voltammetry.**— Rotating disk voltammograms were recorded on a CHI 760 potentiostat. Saturated calomel (SCE) reference half cells (Accumet), Pt mesh counter electrodes and Pt disk working electrodes (Pine,  $0.196 \text{ cm}^2$  area) were used in a standard 3 electrode configuration. Rotation of the working electrode was controlled by a MSRZ Analytical Rotator (Pine). Rotation rates of 200–2500 rpm were used. The working electrode was cleaned between each scan rate by polishing with  $1 \mu\text{m}$  alumina particles (Fisher) on cloth pads. Glassware was dried in a  $100^\circ\text{C}$  oven for at least 30 minutes prior to use. Solutions were purged with Ar to exclude O<sub>2</sub>. For the n and D calculation, all cyclic voltammograms as well as the rotating disk voltammograms were recorded in the same solution and with the same electrode. The  $\text{pH}^*$  was adjusted to 3.0 in order to ensure that all changes in current were related to deuteration rather than changes in bulk concentration of pyridinium.

## Conclusions

An isotopic shift in the potential of the cathodic wave of  $-25$  mV when comparing  $\text{PyrD}^+$  in  $\text{D}_2\text{O}$  to  $\text{PyrH}^+$  in  $\text{H}_2\text{O}$  was observed in cyclic voltammetry at a platinum electrode. The agreement between the experimentally observed potential shift in cyclic voltammetry for a number of weak acids, the expected potential shifts of the weak acids due to the lower  $\text{pK}_a$  of the catalyst upon deuteration, and the DFT calculated shift due to deuteration of  $\text{PyrH}^+$  support the mechanistic hypothesis that the reduction of  $\text{PyrH}^+$  in water at a Pt electrode produces  $\text{H}_{\text{ads}}$ , with the  $\text{pK}_a$  of  $\text{PyrH}^+$  governing the cathodic potential. This mechanism indicates that high Brønsted acid concentration leading to surface hydride formation may be an important paradigm in  $\text{CO}_2$  reduction in addition to its well-known role in proton reduction. Ongoing experimental work is assessing whether the  $\text{H}_{\text{ads}}$  species formed in weak acid reductions on Pt are susceptible to electrophilic attack by  $\text{CO}_2$  and thereby transfer to  $\text{CO}_2$  by proton coupled hydride transfer as suggested by earlier studies.<sup>18</sup>

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