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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/ja4064052 • Publication Date (Web): 23 Aug 2013

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Electrochemistry of Aqueous Pyridinium: Exploration of a Key Aspect of Electrocatalytic Reduction of CO$_2$ to Methanol

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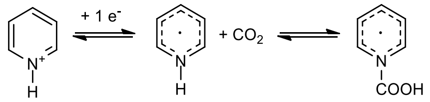
Supporting Information Placeholder

ABSTRACT: The mechanism by which pyridinium (pyrH^{+}) is reduced at a platinum electrode has been a matter of recent controversy. The quasireversible cyclic voltammetric wave observed at -0.58 V vs. SCE at a platinum electrode was originally proposed to correspond to reduction of pyridinium to pyridinyl radical (pyrH$^{\bullet}$). This mechanistic explanation for the observed electrochemistry seems unlikely in light of recent quantum mechanical calculations that predict a very negative reduction potential (-1.37 V vs. SCE) for the formation of pyrH$^{\bullet}$ radical. Several other mechanisms have been proposed to account for the discrepancy in the calculated and observed reduction potentials, including surface adsorption of pyrH$^{\bullet}$, reduction of pyrH^{+} by two electrons rather than one and reduction of the pyrH^{+} proton to a surface hydride rather than a π-based radical product. This final mechanism, which can be described as the inner sphere reduction of pyrH^{+} to form a surface hydride, is found to be consistent with experimental observations.

The electrochemical reduction of CO$_2$ with pyridinium as a catalyst has been reported to occur at low overpotentials to form formic acid and methanol at various interfaces including platinum,[1] palladium,[2] p-GaP[3], iron pyrite[4] and Pt/C-TiO$_2$.[5] We previously suggested that the electrocatalytic mechanism involved a mediated charge transfer process in which pyrH^{+} is first reduced at an electrode surface via a one electron charge transfer, followed by reaction of the electrogenerated pyrH$^{\bullet}$ with CO$_2$ to form a carbamate radical adduct (Scheme 1).[1] This mechanistic proposal has been used to explain the quasireversible cyclic voltammetry of pyrH^{+} at a platinum electrode (Figure 1), which occurs with a standard redox potential of -0.58 V vs. SCE. This potential is consistent with prior literature reports of the electroanalytical reduction of pyrH^{+} in the absence of CO$_2$.[6,7] A mechanism that involves the one-electron reduction of the pyrH^{+} π-system followed by a second electron transfer to the carbamate radical shown in Scheme 1 is consistent with the scan rate dependent current enhancement observed in the cyclic voltammetry of pyrH^{+} under CO$_2$, as well as the first order dependence of current on pyrH^{+} and CO$_2$.[8] The proposed pyridine-CO$_2$ radical carbamate intermediate has been observed via vibrational spectroscopy in the gas phase reaction of CO$_2^{\bullet-}$ and pyridine, supporting the reactivity suggested in Scheme 1.[9]

Recently, a calculation by Keith and Carter provided computational access to the pK$_a$s and redox potentials of the short-lived pyridinyl radical species formed via electroreduction of various substituted pyridiniums in aqueous solution.[10,11] The pK$_a$ for deprotonation of the pyrH$^{\bullet}$ nitrogen in water was calculated to be ~27. This theoretical value has been confirmed by an independent calculation carried out by Musgrave.[12] Such a high pK$_a$ makes deprotonation unfavorable, resulting in a high energy transition state for formation of a carbamate radical intermediate. This conclusion is inconsistent with the low overpotential measured experimentally for the pyrH^{+} catalyzed CO$_2$ reduction at a Pt electrode. Additionally, the reduction potential of pyrH^{+}/pyrH$^{\bullet}$ in solution was calculated to be –1.37 V vs. SCE,[13] 800 mV more negative than the experimentally observed reduction potential at a Pt electrode. Other groups have also calculated similarly high reduction potentials for pyrH^{+} to pyrH$^{\bullet}$.[12,14,15] The discrepancy between these theoretical calculations and the experimentally observed redox potential at a platinium electrode calls into question the existence of pyrH$^{\bullet}$ radical in solution.

Several mechanisms for CO$_2$ reduction with pyridinium catalysis have been proposed given the discrepancies noted above. Possible mechanisms associated with the initial charge transfer to pyrH^{+} include reductive formation of 4,4'-bipyridine from pyrH^{+},[10] reduction of pyrH^{+} by two electrons forming 1,4-dihydropyridine,[13] facilitated carbamate radical formation via a cyclic transition state utilizing bridging water molecules[12] and reduction of CO$_2$ by a surface confined platinum hydride formed by the reduction of the acidic pyridinium proton.[15] Herein, we experimentally examine the proposed pyrH^{+} reduction mechanisms. In addition to the carbamate based mechanism that we previously hypothesized, it is concluded that another plausible mechanism for the observed electrocatalytic process on a platinum electrode proceeds through the direct formation of a platinum hydride via an inner sphere reduction of pyrH^{+}.



Scheme 1. Pyridinium reduction by one electron forming the pyridinyl radical followed by its reaction with CO$_2$ to form a radical carbamate.

Mechanism I: Pyridinyl as the primary reduction product. Explicit experiments were conducted to detect the transient formation of the pyrH$^{\bullet}$ radical from pyrH^{+} in both aqueous and organic solvents. UV-Vis and EPR spectroelectrochemistry were undertaken in an attempt to observe the π-radical. In-situ electrochemical generation of radical species at a Pt electrode was consistently detected by EPR and UV-Vis spectroscopy in aqueous solution at room temperature when 4,4'-bipyridinium was used as the reactant (Figure S1). In addition, a π-radical reduced cyanopyridine derivative has been observed spectroelectrochemically.[19] However, in parallel experiments with pyrH^{+}, no evidence for the formation of the radical pyrH$^{\bullet}$ was observed.

Separately, transient absorption spectroscopy was undertaken and detected the reduction of 4,4'-bipyridinium to 4,4'-bipyrdiyl radical by excited $[Ru(bpy)_3]^{2+}$ ($Ru(III)/Ru(II)^*$ = -0.89 V vs. SCE). In contrast, no formation of $pyrH^\bullet$ was observed in the presence of $pyrH^+$ and excited $[Ru(bpy)_3]^{2+}$ under the same conditions. Stern-Volmer quenching studies were applied using pyridinium or 4,4'-bipyrdinium as the quencher and $[Ru(bpy)_3]^{2+}$ as the luminophore in aqueous solution. A quenching rate constant k_q of $\sim 2\times10^9$ $M^{-1}s^{-1}$ was obtained for 4,4'-bipyridinium, however, negligible quenching was observed by $pyrH^+$.[20] This indicates a redox potential more negative than -0.89 V vs. SCE for $pyrH^+/pyrH^\bullet$. Conversely, we observe that pyridinium does charge transfer quench $[Ir(ppy)_3]$ (ppy = 2-phenylpyridine) ($Ir(IV)/Ir(III)^*$ = -1.73 V vs. SCE, excited state lifetime, τ = 1.9 μs). A Stern-Volmer plot was obtained with a K_{sv} of 116 M^{-1} indicating a k_q of $\sim 10^8$ $M^{-1}s^{-1}$ for $pyrH^+$ quenching (Figure S2). The observation of quenching requires a redox potential for the $pyrH^+/pyrH^\bullet$ less negative than -1.73 V vs. SCE. The spectroelectrochemical and quenching studies together with the theoretical calculations imply electrochemical generation of $pyrH^\bullet$ at -0.58 V vs. SCE in aqueous solution is unlikely to occur via an outer sphere process.

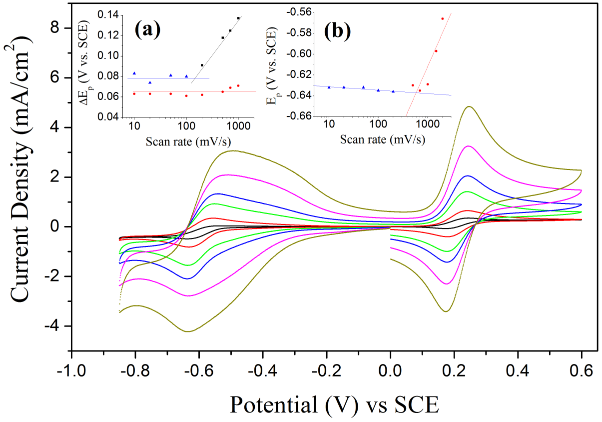


Figure 1. Scan rate dependence of pyridinium reduction on a platinum electrode in the presence of ferrocyanide at 5, 20, 100, 200, 500 and 1000 mV/s, with peak separation vs. log of scan rate for pyridinium (black) and ferrocyanide (red) plotted as inset a. Pyridinium reduction showed a large diffusion limited peak ($E_{1/2}$ = -0.58 V vs. SCE) and prefeatures (ca. -0.4 V vs. SCE) at scan rates above 100 mV/s indicative of a minor adsorptive process. For comparison, ferrocyanide ($E_{1/2}$ = 0.21 V vs. SCE) exhibited reversible electrochemistry (inset a). The pyridinium reduction peak potential shifts more negative with scan rate above 500 mV/s, indicative of quasireversibility. By Gileadi's method,[16,17] the heterogeneous electron transfer rate constant was calculated to be 0.019 cm s^{-1} from the critical scan rate where peak potential begins to shift, 580 mV/s (inset b). This compares well to value for k_{et} of 0.0078 ± 0.0022 cm s^{-1} calculated from digital simulation of the cyclic voltammetry of pyridinium.[8,18]

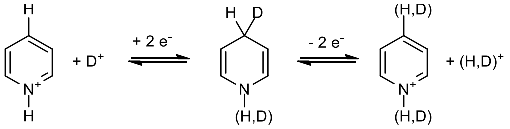
Mechanism II: Surface Adsorbed Pyridinium or Pyridinyl. Keith and Carter suggested that the free energy discrepancy between the calculated and observed reduction potentials might be associated with surface adsorption of pyridinyl radical.[10] Similarly, Musgrave's group suggested that pyridinium adsorption on a platinum electrode could shift the reduction potential anodically relative to that of solution based pyridinium.[12a,b] Strong adsorption manifests itself in cyclic voltammetry as a wave with peak current proportional to scan rate and in the ideal limit, zero separation in oxidative and reductive peak potential. This wave can coexist with a diffusion limited wave, and in that case appears as either prepeaks (adsorbed product) or postpeaks (adsorbed reactant).[21] The primary reduction wave of pyridinium has peak current in cyclic voltammetry proportional to the square root of scan rate and limiting current in rotating disk voltammetry proportional to square root of rotation rate, indicative of a diffusion limited reaction. But, pyridinium reduction at a platinum electrode is more complex than a simple outer sphere electron transfer, as exhibited by the data in Figure 1. At high scan rates (>200mV/s), prepeak shoulders observed on the pyridinium wave suggest the presence of adsorptive processes in addition to the primary diffusive peak. These pre-features are similar to those observed in other acid reductions, such as potassium hydrogen phthalate and acetic acid as well as the reduction of protons from strong acids, indicating the pre-features are not specific to pyridine or its derivatives. (Figure S3). Thus, selective adsorption of pyridinium must be ruled out as the source of the discrepancy.

Mechanism III: A two-electron reduced product. If the reaction resulting in the observed voltammetry is not a one electron reduction of $pyrH^+$ to $pyrH^\bullet$, but is in fact the two electron reduction of $pyrH^+$ to dihydropyridine, then that would lead to a more positive reduction potential. Keith and Carter have calculated the reduction potential of pyridinium to 1,4-dihydropyridine (DHP) to be -0.72 V vs. SCE.[13] To identify the number of electrons transferred in the observed reduction of $pyrH^+$, the peak current in cyclic voltammetry (i_p) and the limiting current in rotating disk voltammetry (i_l) were evaluated. Both i_p and i_l are dependent on the number of electrons (n) as well as the diffusion coefficient (D) of the species being reduced (Equation 1, 2). It is possible using cyclic voltammetry combined with rotating disk voltammetry data to calculate the number of electrons transferred and the diffusion coefficient of the analyte independent of an electrochemical standard in solution. Using plots of i_p vs. $\nu^{1/2}$ and i_l vs $\omega^{1/2}$, values for n and D were calculated (Figure S4). For $pyrH^+$, n = 0.8 and D = 2.1×10^{-5} cm^2s^{-1}. Equations 1 and 2 assume a reversible process[21] which can be approximated for the $pyrH^+$ system in the absence of CO_2. A value of n = 0.8 indicates a one electron transfer is occurring for the diffusion limited peak, precluding the two electron reduction to dihydropyridine. The value less than one can be attributed to the small current corresponding to the cyclic voltammetric prefeatures observed (vida infra).

$$\boldsymbol{i_p = 2.69\times10^5 n^{3/2} A C_O^* D^{1/2} \nu^{1/2}} \qquad (1)$$

$$i_l = 0.62 n F A C_O^* D^{2/3} \nu^{-1/6}\, \omega^{1/2} \qquad (2)$$

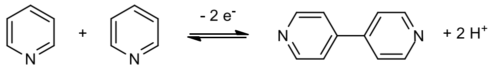
Additionally, if 1,4-dihydropyridine was produced as an intermediate, deuterium exchange at the pyridine 4-position would be expected (Scheme 2). Exhaustive electrolysis at potentials near the peak of the voltammetric wave yields no exchange by proton NMR with either d_5-pyridinium electrolyzed in H_2O or H_5-pyridinium electrolyzed in D_2O.



Scheme 2. Pyridinium reduction to a 1,4-dihydropyridine intermediate in D_2O electrolyte, leading to isotopic scrambling at the 1 and 4 positions.

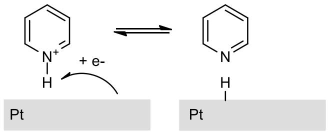
These observations exclude 1,4-dihydropyridine as the product from the voltammetric reduction. To investigate the reactivity of DHP with CO_2, 1,4-dihydropyridine was synthesized,[22] and reacted with CO_2 producing a gel. No reduced CO_2 derived products were detected in the gel. Upon acidification of the gel, CO_2 was released and detected by IR spectroscopy and gas chromatography but again, no reduced products were detected by either IR, GC or NMR (Figure S5). This indicates DHP reacts with CO_2 as a strong base rather than as a reducing agent.

More speculatively, Keith and Carter pondered the possibility that the electrochemistry of pyridinium might involve the transient formation of 4,4'-bipyridine (Scheme 3), followed by rapid dissociation to regenerate pyridinium in solution. They calculated the reduction potential of bipyridinium at a platinum electrode to be -0.58 V vs. SCE and indicated that this may be the active species in the observed electrochemistry. The oxidative coupling of pyridine to form bipyridine has been reported in deareated and anhydrous non-protic organic solvent with Pt particles as catalyst,[23] however this coupling has not been observed in aqueous solution. The quasi-reversibility of the cyclic voltammetric data requires rapid cleaveage of a carbon-carbon bond to regenerate the pyrH$^+$ species, implying formation of a transient bipyridine species is energetically untenable. Additionally, the lack of deuterium exchange of the pyridinium 4-position protons in electrolyses in D_2O argues against the transient formation of bipyridine. Further, the reactivity of sterically hindered 4-*tert*-butylpyridinum would radically differ from pyrH$^+$ if the suggested coupling occurred. But, this is not the case (see Figure 4). Finally, no oxidative two-electron chemistry was detected in the cyclic voltammograms, ruling out the electrochemical formation of bipyridine.



Scheme 3. Formation of 4,4'-bipyridine from oxidative pyridine coupling.

Mechanism IV: Pyridinium as a reagent for Pt-H formation. The mechanisms discussed above focus on the pyridinium π-orbital as the electron acceptor. On a platinum electrode, the proton bound to the pyridine nitrogen is reducible in its own right. The mechanistic possibility of proton reduction on a Pd electrode was previously considered when the electrocatalytic pyridinium reduction of CO_2 was first reported.[2] Batista and coworkers recently provided theoretical support that a hydride formed on the Pt(111) electrode surface might be an important step in the CO_2 reduction mechanism.[15] The calculated redox potential for pyridine-bound proton reduction (Scheme 4) is ca. -0.7 V vs. SCE, well within the range of theoretical error to what has been experimentally observed.



Scheme 4. Inner sphere reduction of a pyridinium-bound proton on a platinum electrode to form a surface hydride.[15]

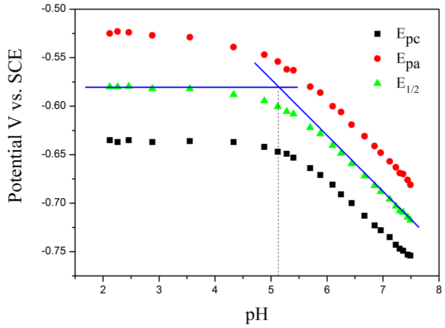


Figure 2. Plot of peak potentials (E_{pc} and E_{pa}) and half wave potential ($E_{1/2}$) versus pH in aqueous solution of pyridinium on a polished platinum electrode.

We examined this pathway experimentally by producing a Pourbaix diagram for pyridinium reduction. The cyclic voltammetry of pyridinium on a platinum electrode was recorded with varying pH. It followed the expected behavior for weak acids[24] in that the half wave potential ($E_{1/2}$) was stable at -0.58 V vs. SCE when pH < pK_a and decreased with a slope of -59 mV when pH > pK_a (Figure 2). To maintain an observable concentration of pyrH$^+$ up to pH = 8 the ratio of pyridinium to pyridine was adjusted by adding pyridine. The peak current was proportional to concentration of pyrH$^+$ at each pH as governed by the acid dissociation equilibrium. Further, when the pH was low enough for comparable concentration of pyrH$^+$ and H_3O^+ (pH = 3, [H_3O^+] = 1 mM), a wave representing hydronium reduction at ca. -0.4 V vs. SCE was observed alongside that of pyridinium reduction at -0.58 V vs. SCE (Figure 3). This wave continued to increase as the pH decreased. This clearly indicates that the wave at -0.58 V vs. SCE is due to pyrH$^+$ and not H_3O^+ reduction. The plateau redox potential at pH < pK_a indicated that the reduction of pyrH$^+$ occurs in an electrochemical process that is unrelated to the hydronium concentration in solution. As expected for a Pourbaix diagram, the extrapolated lines for the invariant and pH-dependent regions intersect at pH = pK_a = 5.2.

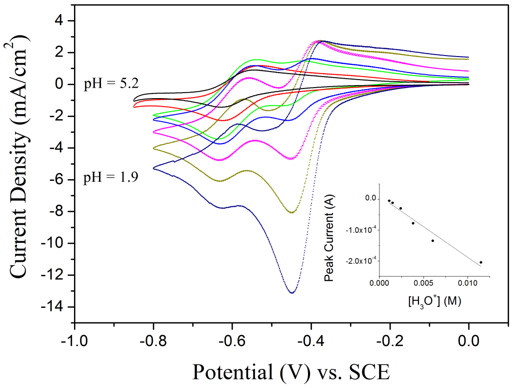


Figure 3. Separate processes for pyridinium and hydronium reduction were observed in cyclic voltammograms of 10 mM pyridine at 100 mV/s at pH = 1.9 2.2, 2.4, 2.6, 2.8, 3.6 and 5.2. When pH was less than the pK_a of pyridinium, the peak current was constant due to unchanging pyridinium concentration. At pH = pK_a = 5.2, the peak current was reduced by half due to the lower pyridinium concentration. The hydronium reduction wave appeared at sufficiently high H_3O^+ concentration (~1 mM, pH = 3) and the peak current increased linearly with [H_3O^+] (inset).

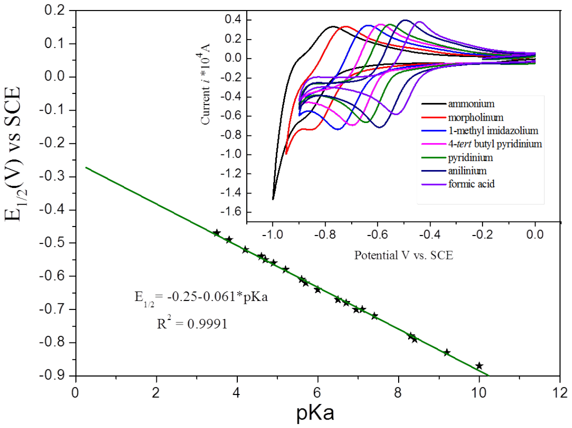


Figure 4. Plot of half wave potential ($E_{1/2}$) vs. pK_a of weak acids in aqueous solution on a Pt disc electrode. Inset is cyclic voltammetry of typical weak acids (in order: ammonium, morpholinium, 1-methylimidazolium; 4-*tert*-butylpyridinium; pyridinium, anilinium, and formic acid) reduction on an alumina polished Pt electrode in 0.5 M KCl aqueous solution at pH=3.4 (for each acid: pH < pKa and scan rate = 100 mV/s).

In order to understand the effect of pK_a on the potential of catalysis we obtained reversible cyclic voltammetric redox waves for over 20 weak acids of varying structure: pyridinium derivatives, aromatic and non-aromatic acids such as amines, phenols, carboxylic acids etc. (Table S1). The plateau half wave potentials were measured and plotted versus their pK_a values (Figure 4). A linear relationship was readily obtained with a slope of ca. – 61 mV. Extrapolated to pH = 0, this line intersected the potential axis at -0.25 V vs. SCE, in good agreement with the standard hydrogen redox potential (-0.24 V vs. SCE). This experiment clearly indicated that π-orbital reduction is not necessary for the observation of reversible waves on Pt electrode. Any weak acid with a suitable pK_a results in an analogous redox wave. Fittingly, $pyrH^+$ follows this weak acid reduction trend, with a observed redox potential of -0.58 V vs. SCE and a calculated redox potential of -0.57 V vs. SCE at pK_a = 5.2 from the weak acid reduction equation.

$$E_{1/2} = -0.061 \times pK_a - 0.25 \qquad (3)$$

This experimentally obtained equation can be readily thermodynamically derived for proton reduction from a weak acid (Equation 4) by combination of Equations 4a-c. This equation explains the general weak acid reduction on Pt electrodes in aqueous solution. Similar relationships have been derived in studies of pK_a vs. reduction potential of weak acids on platinum electrodes in aqueous[25], organic[26] and ionic liquid media.[27]

$$\mathrm{H_3O^+ + e\text{-} \rightleftharpoons H_{(Pt)} + H_2O}$$

$$E_{H^+/H_{(Pt)}} = -(G_{H_{(Pt)}} + G_{H_2O} - G_e - G_{H_3O^+})/nF \qquad (4a)$$

$$\mathrm{HA + H_2O \rightleftharpoons H_3O^+ + A^-}$$

$$G_{A^-} + G_{H_3O^+} - G_{H_2O} - G_{HA} = -RT\ln K_a = 2.303\mathrm{RTpKa}$$
(4b)

$$\mathrm{HA + e\text{-} \rightleftharpoons H_{(Pt)} + A^-}$$

$$E_{HA/H_{(Pt)},A^-} = -(G_{H_{(Pt)}} + G_{A^-} - G_e - G_{HA})/nF \qquad (4c)$$

$$E_{HA/H_{(Pt)},A^-} = E_{H^+/H_{(Pt)}} - (0.059/n) * pK_a \qquad (4)$$

Based on the data presented here, pyridinium π-orbital based reduction is not occurring at a platinum electrode, however, the importance of this reduction pathway should not be ignored for other pyridinium derivatives. For example, 4-4'-bipyridinium can be reduced to form a π-radical species (Figure S1). For aromatic weak acids on a platinum electrode, two different reduction pathways are thus possible (Figure S6): thfe reduction of proton to a surface hydride and, alternatively, the π-system reduction. The π system reduction may be favored at electrode materials where the proton reduction is kinetically unfavorable.

In conclusion, we have experimentally investigated the mechanisms proposed to explain the pyridinium redox potential discrepancy between electrochemical observations and theoretical calculations. The suggested intermediates of 4,4'-bipyridine and 1,4-dihydropyridine by Carter's group and surface adsorbed pyridinium or pyridinyl by Musgrave's and Carter's groups are not strongly supported by the available experimental evidence. On the other hand, pyridinium reduction unambiguously follows the trend of any other weak acid's reduction at a platinum electrode as given by Equation 4. This pathway is consistent with Batista group's theoretical insight into the formation of an interfacial platinum hydride for the initial step of pyridinium reduction. Batista has further suggested that the surface platinum hydride then reduces a CO_2 that is hydrogen bonded to a pyridinium species via the CO_2 oxygen.[15] This aspect of the mechanism cannot be interrogated electrochemically, and we are devising spectroscopic tools to further probe the reaction dynamics. An intriguing alternative to the Batista proposal is a mechanism that utilizes the surface hydride to carryout a proton coupled hydride transfer to an equilibrium carbamate formed between CO_2 and pyridine.

ASSOCIATED CONTENT

Supporting Information

Experimental details and spectral data. 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 interests.

ACKNOWLEDGMENT

We acknowledge support by the Air Force Office of Scientific Research through the MURI program under AFOSR Award No. FA9550-10-1-0572 and the NSF under grant No. CHE-0911114. EZ acknowledges support in part by the Department of Energy Office of Science Graduate Fellowship Program, made possible by the American Recovery and Reinvestment Act of 2009, administered by ORISE-ORAU under contract no. DE-AC05-06OR23100. We thank Dr. Paolo Stufano for helpful discussions.

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(12) (a) Lim, C.-H.; Holder, A. M.; Musgrave, C. B. *J. Am. Chem. Soc.* **2013**, *135*, 142. (b) This mechanism is expected to be very surface sensative. And consistent with this mechanism, we find changes in the cyclic voltammetric response as the electrode material is changed (Au, C, Ni, and In have been screened). However, only the (111) platinum surface have been considered theoretically at this point and thus, it is not possible to evaluate our experimental data against a quantitative theoretical prediction.
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