J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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Theoretical Insights into Pyridinium-Based Photoelectrocatalytic Reduction of CO_2

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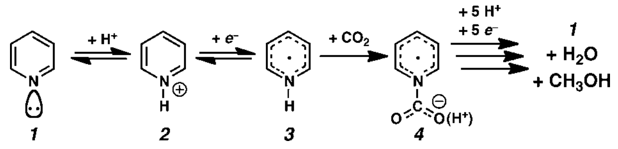
Supporting Information

ABSTRACT: The role of pyridinium cations in electrochemistry has been believed known for decades, and their radical forms have been proposed as key intermediates in modern photoelectrocatalytic CO_2 reduction processes. Using first-principles density functional theory and continuum solvation models, we have calculated acidity constants for pyridinium cations and their corresponding pyridinyl radicals, as well as their electrochemical redox potentials. Contrary to previous assumptions, our results show that these species can be ruled out as active participants in homogeneous electrochemistry. A comparison of calculated acidities and redox potentials indicates that pyridinium cations behave differently than previously thought, and that the electrode surface plays a critical (but still unknown) role in pyridinium reduction. This work substantially alters the mechanistic view of pyridinium-catalyzed photoelectrochemical CO_2 reduction.

Growing populations with dwindling fossil fuel resources stimulate the need for efficient and practical sustainable energy sources. Recently, Bocarsly and co-workers reported electrochemical reduction of CO_2 selectively to methanol using a p-type GaP photoelectrochemical cell and a pyridinium catalyst.[1] While quantum and optical conversion efficiencies are not yet high enough for commercial purposes, the fact that such highly endoergic chemistry can be driven photoelectrochemically at underpotentials (or at least requiring low overpotentials) renders this chemistry a big step forward toward recycling CO_2 emissions back into the carbon-fuel economy.

Scheme 1 illustrates the initial steps of the proposed mechanism for this process.[2] The key component of the mechanism involves a series of one-electron shuttling mechanisms whereby pyridine (Py, **1**) in acidified water accepts a proton to form pyridinium (**2**), which is then reduced to form pyridinyl radical (**3**). **3**, in turn, is expected to be a strong reductant capable of reducing CO_2 to formic acid, formaldehyde, and finally methanol. Very high faradaic yields (~99%) show this process is selective toward methanol formation.[1] Notably, a radical carbamate species (**4**) is also proposed as a key intermediate in this mechanism.[3]

Scheme 1. Postulated Six-Electron Reduction Process of CO_2 to Methanol Catalyzed by Pyridinium [a]



[a] As reported in ref 2.

Pyridinium reduction has been attributed to a cyclic voltammetry reduction peak at −0.58 V versus the saturated calomel electrode (SCE) for Pt electrodes in acidified water.[2] Pyridinium-catalyzed CO_2 reduction has been considered primarily a homogeneous process,[2,4] but some experimental observations have indicated some surface dependencies. The pyridinium-catalyzed reaction proceeds with both Pd-[4] and Pt-electrodes[2,3] as well as semiconductor p-GaP electrodes,[1] but pyridinium shows no discernable reduction current with glassy carbon.[2] Furthermore, kinetics studies found the rate of CO_2 reduction plateaus at pyridinium concentrations greater than 8 mM, indicating either that CO_2 is the limiting reagent at these conditions or that the surface plays a noninnocent role in this reaction.[3] Curiously, two independent measurements that purported to examine the related process of **3** + **3** coupling to form H_2 found rate constants differing by more than 8 orders of magnitude; studies in acidified water[2] report $k_{Hy} = 2.9\ M^{-1}\ s^{-1}$, while studies in aqueous 2-propanol/acetone solutions[5] report $k_{Hy} = 7 \times 10^8\ M^{-1}\ s^{-1}$. The proposed mechanism has also attracted other research efforts to understand this chemistry. Johnson and co-workers characterized the vibrational spectra of the anionic form of **4** in gas phase CO_2 clusters.[6] Tossell used CBS-QB3 calculations with the conductor-like polarizable continuum model (CPCM) solvation approach to calculate homogeneous redox potentials and reaction free energies for Py, pyridinium, and the radical carbamate under the influence of different substituents.[7] Tossell noted that since the reduction potentials of these species are less negative than that for CO_2 alone, all species could be considered reduction catalysts. However, it is peculiar that Tossell's calculated redox potential for **2** (−1.44 V vs SCE) is nearly 1 V more negative than the experimentally obtained potential (−0.58 V vs SCE) for what is believed to be the same process.[2] Redox potentials have been calculated from first principles with reasonable accuracies (within ~0.3 V) for more than a decade,[8−10] so errors greater than 0.5 V may be a sign of mistaken characterization of a chemical system either by theory or by experiment.

Received: January 5, 2012
Published: April 23, 2012

These puzzling electrochemical data motivated us to use theory to attempt to better explain this chemistry. Our calculations were run using the GAMESS-US code.[16,17] Gas phase calculations employed unrestricted density functional theory (DFT) with the Becke 3-parameter, Lee−Yang−Parr (B3LYP) exchange-correlation functional[18,19] and the Dunning aug-cc-pVDZ basis set.[20,21] Zero-point energies and thermal corrections were calculated with the standard harmonic oscillator, ideal gas, and rigid rotor approximations. Solvation energies were computed using the CPCM approach with molecular cavities defined by simplified united atom Hartree−Fock (SUAHF) radii,[22] and DFT-B3LYP/aug-cc-pVDZ electron densities. Our solvation calculations omitted empirical nonelectrostatic energy contributions (cavitation, dispersion, repulsion), used one explicit water in a cluster-continuum approach,[23,24] and used empirical values for the proton gas phase (−6.3 kcal/mol)[25] and aqueous phase solvation (−265.9 kcal/mol)[26] free energies. We extensively benchmarked this calculation scheme across a data set of 22 differently substituted pyridinium cations, testing the effects of different basis sets, continuum solvation models, user-defined parameters, and solvation energy definitions.[11] This approach was found to be the most accurate compared to experimental gas phase and aqueous phase deprotonation data, with predicted pK_as having mean-unsigned errors (MUEs) = 0.9 pK_a units with maximum errors of 2.1 pK_a units. Using the same approach without the explicit water produced MUEs of 1.1 pK_a units with maximum errors of 3.5 pK_a units. We caution against using these exact parameters without further testing except for systems involving deprotonations from a Py moiety.

Figure 1a shows the excellent correlation between theory and experiment for gas phase pyridinium deprotonations using our calculation scheme. Figure 1b shows error cancellation due to the solvation method leads to smaller errors than in gas phase calculations. Again, a satisfactory R^2 value shows a linear correlation, though the slope of the linear fit reaffirms room for improvement in the CPCM solvation model that has been noted elsewhere.[27] Notably, comparisons between pyridinyl and pyridinium deprotonations show no correlation whatsoever. In contrast to pyridinium, pyridinyl pK_as are very high (typically greater than 20, with **3** having a pK_a of ∼27, see Supporting Information).

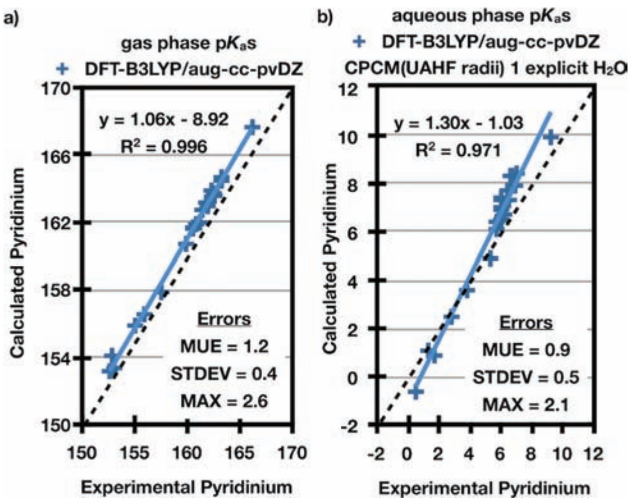


Figure 1. Gas phase and aqueous phase deprotonation energies for substituted pyridinium cations at room temperature (energies expressed in pK_a units: $\Delta G_{298}/2.303RT$). The data set involves a collection of mono- and di-substituted methyl, amino, chloro, and formyl groups (see ref 11) referenced against experimental gas and solution phase data (see refs 12−15).

These predictions have serious implications for the mechanism of pyridinium-catalyzed CO_2 reduction. If the formation of **4** were the rate-determining step as inferred from kinetics,[3] then the deprotonation of **3** should be a reasonable indicator for the overall reduction reaction. On the basis of our calculations, *pyridinyl deprotonations should not be facile at all.* Therefore, another factor must be playing a role in this chemistry. To study this discrepancy more deeply, we calculated standard reduction potentials for differently substituted pyridinium molecules.

Our calculation scheme follows that of Hughes and Friesner,[9] with two minor differences. First, in lieu of using an empirical value for the absolute value of the standard hydrogen electrode (SHE), we reference the pH-dependent proton-coupled electron transfer (PCET) reductions implicitly to the SHE with a calculated energy for H_2.[28] Second, pH-independent, one-electron redox potentials are then anchored with respect to the PCET redox potential at the calculated pK_a for the species. More calculation details can be found in the Supporting Information. Figure 2 shows our results from those calculations.

Figure 2a shows a large difference between the observed reduction potential for the CO_2 reduction catalyst and the calculated homogeneous redox potentials for pyridinium (−0.58 vs −1.44 V, respectively). Our calculated pK_a for **2** was close to the experimental value (calculated = 4.9, experiment = 5.3). Since the experimental pH is also 5.3, it can be assumed that at experimental conditions [**1**] = [**2**]. Therefore, we may also consider whether the observed reduction potential reflects a PCET directly from Py. We predict this to occur at −1.47 V (at pH = 5.3), nearly identical to our pH-independent redox potential for **2** (−1.45 V). Coincidentally, the latter redox potential is also nearly identical to Tossell's one-electron redox potential of −1.44 V,[7] despite the significantly different approach used here. To confirm that our theoretical calculations are valid, we also calculated redox potentials for N-substituted pyridinium species with a wide range of experimentally known redox potentials.[29] The experimental reductions were done in acetonitrile; our calculated reductions employed the CPCM model with no explicit solvent molecules and standard solvent parameters for acetonitrile (ε = 35.69 and probe radius = 2.18 Å, solvation parameters from ref 30). As was found in water solvent, experiment and theory differ substantially for the redox potential of unsubstituted pyridinium. The calculated redox potentials for other pyridinium species, however, agree to within 0.2 V of experiment (Figure 2b), validating our theoretical approach and suggesting that the measured potential is reflecting something other than the reduction of unsubstituted pyridinium.

Two points disfavor the role of **3** in solution as an active participant in CO_2 reduction. First, the very high calculated pK_a values render it and other N-protonated pyridinyl species inactive. Second, the one-electron and PCET reduction potentials are both ∼1 V more negative than the potential attributed to pyridinium reduction with Pt electrodes. Our reduction potential is supported by earlier published reports that found pyridinium reduction occurred at ∼-1.5 V on a dropping Hg electrode in acetonitrile[31] and a 1940s study in acidified water.[32] This high redox potential is yet more

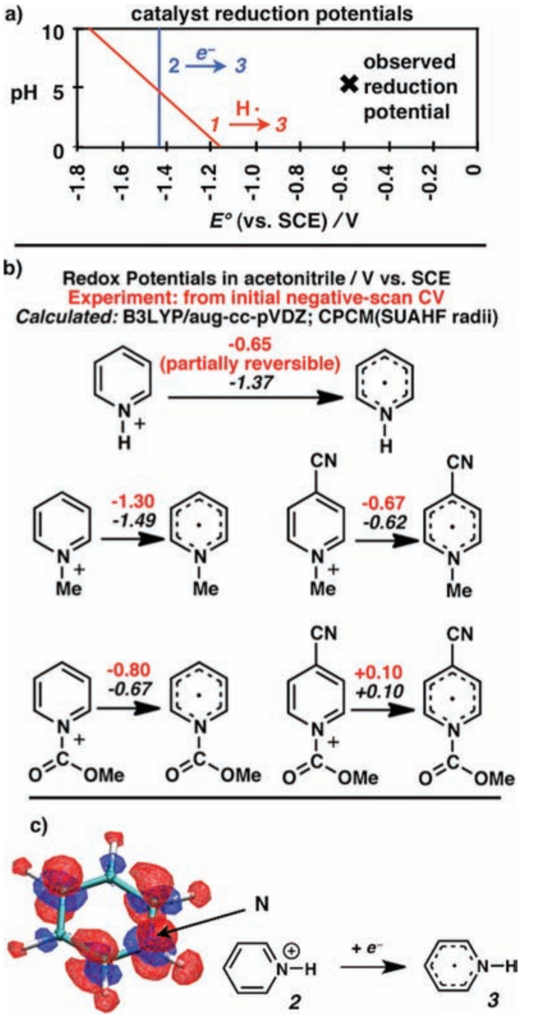
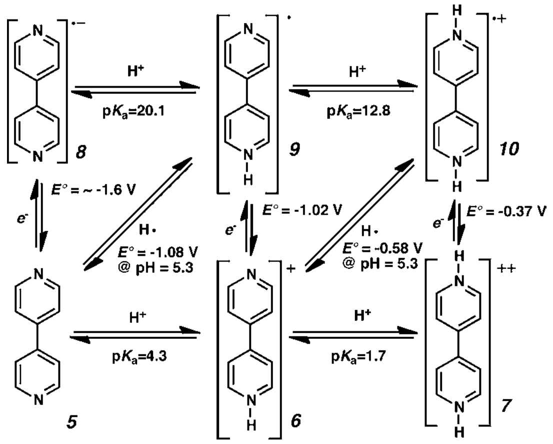


Figure 2. (a) One-electron (blue line) and PCET (red line) homogeneous standard reduction potentials involving pyridine (**1**) and pyridinium (**2**). Very large deviations from the observed reduction potential suggest the actual mechanism cannot involve reduction of pyridinium to pyridinyl in homogeneous solution. (b) Calculated and experimental[29] one-electron redox potentials for differently substituted pyridinium species in acetonitrile. Unsubstituted pyridinium is a significant outlier compared to other homogeneous pyridinium reductions. (c) Density difference plots for adding an electron to **2** to form **3**. Red denotes added electron density; blue denotes reduced electron density. Added electron density occupies space corresponding to an antibonding π^* orbital; note the σ-system is polarized by the added π-electron, a phenomenon well-known in the isoelectronic benzene molecule.

reasonable after examination of electron density changes upon adding an electron to **2** to form **3** (Figure 2c). We find that the added electron resides in an antibonding π^* orbital, and hence, one should expect substantial energy is required to reduce **2** into **3**, consistent with the very high reduction potential we predict. By contrast, strongly electron-withdrawing groups on the Py ring dramatically reduce the pyridinium redox potential (Figure 2b), by stabilizing the π^* orbital.

Our calculations rule out the possibility of homogeneous pyridinium reduction or PCET to pyridinyl, so another process must be in play. We have begun to investigate pyridinium and CO_2 reduction processes on surfaces, but since 4,4′-bipyridine (BPy) is reduced in the presence of glassy carbon electrodes,[2] we also calculated its pK_as and redox potentials (Scheme 2, see Supporting Information for more calculation details). In general, our results correspond favorably with measured pK_as and reduction potentials for BPy.[33,34]

Scheme 2. Reduction Scheme for 4,4′-Bipyridine (BPy) Species[a]



[a] All redox potentials reported in V vs SCE.

What remains unclear is the cause for the observed reduction peak at −0.58 V previously attributed to pyridinium reduction. It may correspond to heterogeneous reduction of **2** → **3**; however, Figure 2b indicates that the surface would need to exhibit strongly electron-withdrawing character to result in such a large shift in the reduction potential. Scheme 2 predicts that the PCET process **6** → **10** has exactly the same redox potential as the measured one, and **10**'s pK_a may be low enough to facilitate proton−CO_2 exchange to form a carbamate. Although oxidative coupling is unexpected at a cathode and the homogeneous coupling of two aqueous-phase **1** molecules into an aqueous-phase **5** with gaseous H_2 is quite unfavorably 0.63 eV uphill (see Supporting Information), this process potentially could be favorable on a surface. If BPy were to form and detach from the surface, it would certainly be short-lived due to the sizable thermodynamic driving force of the reduction potential that would return it to two Py. We reiterate that it has not yet been established how the surface plays a role in this chemistry, and to the best of our knowledge, there has been no experimental evidence of BPy being the functioning catalyst in these reactions. Our results do show, however, that *under no circumstances can homogeneous pyridinyl radicals in solution be considered active catalysts for CO_2 reduction.*

In conclusion, to better understand puzzling experimental and theoretical observations regarding pyridinium-catalyzed photoelectrocatalytic CO_2 reduction, we used quantum chemistry to determine energies of molecular species that have been proposed as intermediates in its mechanism. We predict pyridinyl pK_a values to be much higher than pyridinium ones, such that pyridinyls are very unlikely to undergo proton−CO_2 exchange to form carbamates. We also found that reduction potential for unsubstituted pyridinium is much more negative than anticipated. On the basis of these results, *pyridinyl species should not be expected to form in homogeneous solutions, and it is highly unlikely they would participate in any chemistry unless very high potentials are applied*. Our work does not rule out that adsorbed pyridinyl species participate in this chemistry, and we also note that the acidities of the protonated radical 4,4′-bipyridinyl and the redox potentials of 4,4′-bipyridinium make BPy a solid candidate to catalyze CO_2

reduction. Furthermore, Py coupling to form BPy should be considered more likely than homogeneous pyridinium reduction. Detecting BPy species in solution or characterizing Py intermediates on surfaces would readily identify the active catalyst for this chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further calculation details, Cartesian coordinates, and energies of species discussed in the text. 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.

■ ACKNOWLEDGMENTS

This work was funded by the MURI program under AFOSR Award No. FA9550-10-1-057. The authors thank Aaron Appel, Donald Camaioni, and Dmitriy Polyanskiy for literature references and Amanda Morris, Kyle Grice, Andrew Bocarsly and his group for useful discussions.

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