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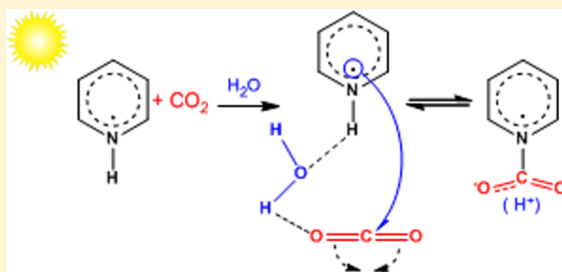
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# Homogeneous Reduction of CO<sub>2</sub> by Photogenerated Pyridinyl Radicals

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**ABSTRACT:** We report that 1-hydropyridinyl radicals (1-PyH•) photogenerated in solution react with dissolved CO<sub>2</sub> en route to its 2e<sup>−</sup> reduction into carboxylic acids. The 254 nm excitation of pyridine (Py) in deaerated 2-PrOH/H<sub>2</sub>O mixtures saturated with 1 atm of CO<sub>2</sub> yields a suite of products, among which we identified Na(HCOO)<sub>2</sub><sup>−</sup> (*m/z*<sup>−</sup> = 113), C<sub>3</sub>H<sub>6</sub>NCOO<sup>−</sup> (*m/z*<sup>−</sup> = 124), and C<sub>3</sub>H<sub>10</sub>O<sub>2</sub>NCOO<sup>−</sup> (*m/z*<sup>−</sup> = 160) species by electrospray ionization mass spectrometry. These products demonstrably contain carboxylate functionalities that split CO<sub>2</sub> neutrals via collisionally induced dissociation. We infer that 1-PyH• [from (1) <sup>3</sup>Py\* + 2-PrOH → 1-PyH• + •PrOH] adds to CO<sub>2</sub>, in competition with radical–radical reactions, leading to intermediates that are in turn reduced by •PrOH into the observed species. The formation of carboxylates in this system, which is shown to require CO<sub>2</sub>, Py, 2-PrOH, and actinic radiation, amounts to the homogeneous 2e<sup>−</sup> reduction of CO<sub>2</sub> by 2-PrOH initiated by Py\*. We evaluate a rate constant (2) *k*<sub>2</sub>(1-PyH• + CO<sub>2</sub> → •Py-1-COOH) ≈ 0 (10) M<sup>−1</sup> s<sup>−1</sup> and an activation energy *E*<sub>2</sub> ≥ 9 kcal mol<sup>−1</sup> that are compatible with thermochemical estimates for this reaction.



## INTRODUCTION

The impact of fossil fuel combustion emissions on Earth's climate would be alleviated by an ideal process that captures atmospheric CO<sub>2</sub> at ~400 ppm levels and releases it in concentrated form with minimum energy expenditure and capital investment,<sup>1–6</sup> followed by its reductive conversion into fuels and/or chemical feedstocks via an artificial photosynthetic device using inexpensive materials and driven by sunlight.<sup>7–14</sup> The endoergic reduction of CO<sub>2</sub> into organic matter at significant rates, however, is challenging, perhaps as best attested by the fact that evolution took ~2 billion years to develop photosynthesis.<sup>15</sup> The negative electron affinity of CO<sub>2</sub> in the gas phase<sup>16</sup> translates in solution into a one-electron transfer that converts linear CO<sub>2</sub> into bent CO<sub>2</sub><sup>•−</sup> both hindered by unfavorable thermodynamics *E*<sup>o</sup>(CO<sub>2</sub>/CO<sub>2</sub><sup>•−</sup>) = −2.14 V (versus SCE) and very slow self-exchange rates.<sup>17</sup> The two-electron (hydride) transfer into HCOO<sup>−</sup> (*E*<sup>o</sup> = −0.55 V versus SCE) or the stabilization of CO<sub>2</sub><sup>•−</sup> into bound intermediates appear to be more favorable pathways to initiate the reduction of CO<sub>2</sub> toward CH<sub>3</sub>OH and CH<sub>4</sub>.

The chemical stabilization of CO<sub>2</sub><sup>•−</sup> may have already been achieved in the pyridine (Py)-catalyzed electroreduction of CO<sub>2</sub>.<sup>18,19</sup> The originally proposed mechanism, in which 1-hydropyridinyl radicals (1-PyH•),<sup>20–22</sup> from the electrochemical reduction of pyridinium (PyH<sup>+</sup>), react homogeneously with dissolved CO<sub>2</sub> to produce a carbamyl intermediate, however, is held in contention.<sup>19,23–26</sup> It has been challenged by calculations predicting a reduction potential *E*<sup>o</sup>(PyH<sup>+</sup>/PyH•) ≈ −1.4 V (versus SCE)<sup>23</sup> that is significantly more negative than the reported *E*<sup>o</sup> = −0.58 V experimental

value.<sup>19</sup> On this premise, it was asserted that “under no circumstances can homogeneous pyridinyl radicals in solution be considered active catalysts for CO<sub>2</sub> reduction”.<sup>23</sup> It should be pointed out, however, that such a conclusion implicitly assumes that the discrepancy can *only* be accounted for by the adsorptive stabilization of 1-PyH• on the cathode. Other explanations, however, are possible.<sup>26</sup> There is evidence that partial charge transfer from an unpolarized electrode to preadsorbed PyH<sup>+</sup> would also render *E*<sup>o</sup>(PyH<sup>+</sup>/1-PyH•) less negative than the calculated −1.4 V value.<sup>25</sup> It is therefore possible that the electrochemical reduction of PyH<sup>+</sup> on Pt at *E*<sup>o</sup> = −0.58 V could release 1-PyH• into the bulk electrolyte, as originally proposed.<sup>19</sup> The outstanding issue at this point seems to be whether 1-PyH• in fact reacts with CO<sub>2</sub> homogeneously in water. Here, we address this key question and report experiments in which 1-PyH• is generated photochemically in situ in 2-propanol (2-PrOH)/water mixtures containing dissolved CO<sub>2</sub>.

## EXPERIMENTAL SECTION

All reagents were of chemical grade. Py and 2-PrOH (Sigma-Aldrich) and carbon dioxide (Air Products) were used as received. Py solutions in 10% (v/v) 2-PrOH/Milli-Q water mixtures were adjusted to pH 3 with HCl, where Py (*pK*<sub>a</sub> =

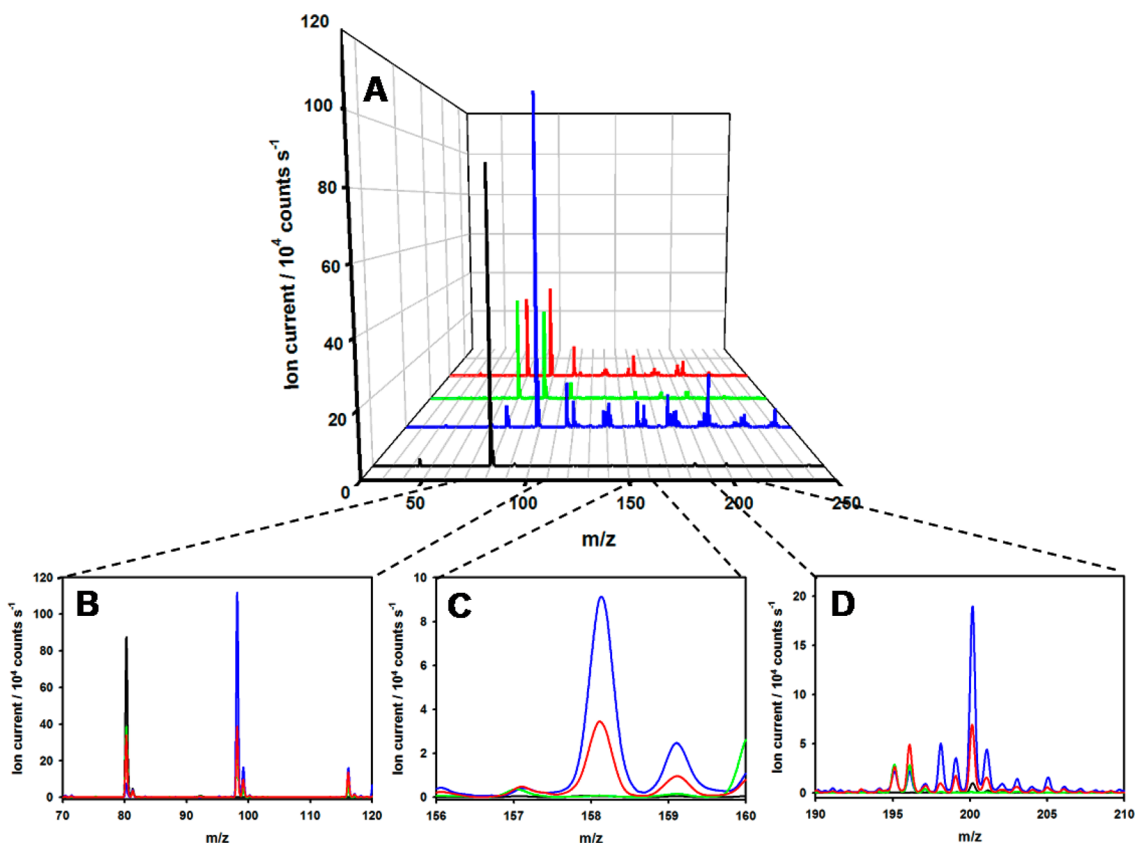
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The reaction scheme illustrates the photochemical conversion of pyridine ( $C_5H_5N$ , 79 Da) into various products. The process begins with the excitation of pyridine at 254 nm to a triplet state ( $3\pi$ ), which then undergoes various reaction pathways:

- Pathway 1:** Reaction with  $H_2O$  to form a dihydro-pyridine intermediate ( $C_5H_7NO$ , 97 Da), which can further react with  $H_2O$  to yield a dihydro-pyridine-2-ol ( $C_5H_9NO_2$ , 115 Da).
- Pathway 2:** Reaction with  $\bullet PrOH$  and  $H$  atom to form a dihydro-pyridine-2-ol ( $C_8H_{15}NO_2$ , 157 Da).
- Pathway 3:** Reaction with  $\bullet PrOH$  and  $H$  atom to form a dihydro-pyridine-2-ol ( $C_{11}H_{21}NO_2$ , 199 Da).
- Pathway 4:** Reaction with  $\bullet PrOH$  and  $H$  atom to form a dihydro-pyridine-2-ol ( $C_8H_{13}NO$ , 139 Da).
- Pathway 5:** Reaction with  $CO_2$  and  $H$  atom to form a dihydro-pyridine-2-ol ( $C_6H_7NO_2$ , 125 Da), which can further react with  $2 H_2O$  to yield a dihydro-pyridine-2,6-diol ( $C_6H_{11}NO_4$ , 161 Da).

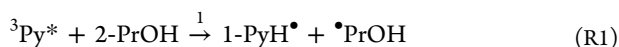


**Figure 1.** (A) Positive ion ESI mass spectra of 10 mM Py solution in H<sub>2</sub>O or in 10%(v/v) 2-PrOH/H<sub>2</sub>O under various conditions. (Black trace) Preirradiated solutions. ESI mass spectra of solutions irradiated at 254 nm for 1 h follow. (Blue trace) In 10%(v/v) 2-PrOH/H<sub>2</sub>O. (Red trace) In 10%(v/v) 2-PrOH/H<sub>2</sub>O saturated with 1 atm of CO<sub>2</sub>. (Green trace) In neat H<sub>2</sub>O, saturated with CO<sub>2</sub>. (B–D) Zoom into the mass ranges where the  $m/z^+ = 80, 98, \text{ and } 116, 158, 200$  products appear, respectively.

5.3) is largely present as pyridinium  $\text{PyH}^+$ . Photolysis experiments were performed in a sealed, custom-made glass reactor equipped with a silica sleeve housing a Pen-Ray (P/N 90–0012) Hg lamp emitting  $\sim 3 \times 10^{15}$  254 nm photons  $\text{s}^{-1}$ ,<sup>27</sup> whose output was filtered with a short-pass filter that blocks spurious 365 nm emissions. Py/2-PrOH/ $\text{H}_2\text{O}$  solutions (10  $\text{cm}^3$ ) were thermostated at  $(25 \pm 2)^\circ\text{C}$ , degassed in situ by freezing and thawing cycles under vacuum, and finally saturated with  $\text{CO}_2$  at 1.0 atm prior to photolysis. Liquid samples were extracted through a silicone rubber septum before and after 1 h photolysis and analyzed via direct infusion (via a syringe pump at 50  $\mu\text{L}/\text{min}$  through a grounded stainless steel injector) electrospray ionization (ESI) mass spectrometer (HP 1100 LC/MSD) operated in positive and negative ion modes.<sup>28,29</sup> Typical conditions for the ESI mass spectrometric analysis were: drying  $\text{N}_2$  gas at  $325^\circ\text{C}$  injected at 8 L/min and a polarizing voltage of  $\pm 2.5$  kV. Collisionally induced fragmentation  $\text{MS}^2$  spectra of anions and cations were obtained at 10 and 50 V acceleration voltages, respectively.

## RESULTS AND DISCUSSION

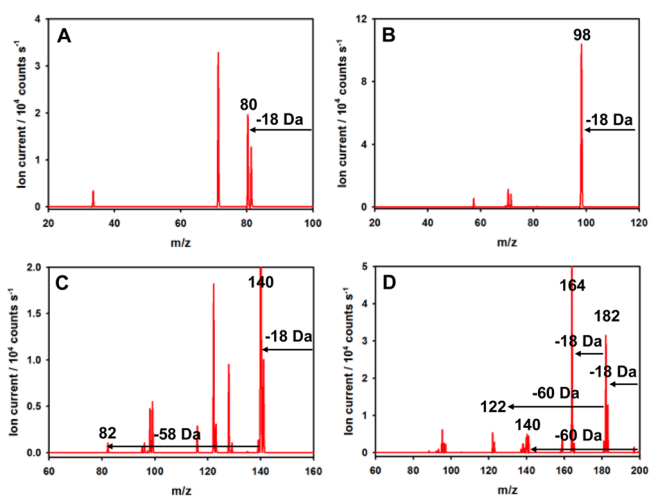
Only Py/ $\text{PyH}^+$  ( $\lambda_{\text{max}} = 254$  nm,  $\epsilon_{\text{max}} \approx 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) absorb significantly at 254 nm in freshly prepared 10% (v/v) 2-PrOH ( $\lambda_{\text{max}} = 205$  nm,  $\epsilon_{\text{max}} \approx 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ )/water solutions.<sup>30,31</sup> The 254 nm photolysis of Py has been previously investigated in water<sup>30</sup> and 2-PrOH.<sup>32–34</sup> In water, Py is converted into a detectable (Dewar) valence isomer, which hydrolyzes thermally into 5-amino-2,4-pentadienal (and its gem-diol) with an overall quantum yield of  $\sim 0.06$  (see Scheme 1). The photolysis of Py in 2-PrOH proceeds via excited triplet states  $^3\text{Py}^*$  that can H-abstract from 2-PrOH, leading to 1-hydropyridinyl  $\text{PyH}^\bullet$  and ketyl  $^\bullet\text{PrOH}$  [ $^\bullet\text{C}(\text{OH})(\text{Me})_2$ ] radicals, reaction R1<sup>34</sup>



Since  $^\bullet\text{PrOH}$  readily transfers a H atom to  $\text{Py}$ ,<sup>32</sup> the overall stoichiometry of reaction R1 is actually  $2\text{Py} + h\nu + 2\text{-PrOH} \rightarrow 2\text{PyH}^\bullet + \text{Pr}=\text{O}$ .

In accordance with the preceding considerations, we found that the positive ion ESI mass spectra of the products of the photolysis of Py in water display, in addition to  $m/z^+ = 80$  ( $\text{PyH}^+$ ), intense  $m/z^+ = 98$  and 116 signals that correspond to protonated species of mass 97 and 115 Da resulting from the addition of one and two water molecules to Py, respectively (Figure 1 and Scheme 1).  $\text{MS}^2$  spectra of both  $m/z^+ = 98$  and 116 ions reveal  $-17$  (OH) and  $-18$  ( $\text{H}_2\text{O}$ ) Da neutral losses, as expected (Figure 2). Note that all even mass ions must carry a N atom, that is, they derive from Py.

The photolysis of Py in 10% (v/v) 2-PrOH/ $\text{H}_2\text{O}$  mixtures generates additional intense peaks at  $m/z^+ = 140$  and 158 from the protonation of  $139 = 80$  ( $\text{PyH}^\bullet$ ) +  $59$  ( $^\bullet\text{PrOH}$ ) and  $157 = 139 + 18$  neutrals, respectively, which ensue from the recombination of  $1\text{-PyH}^\bullet$  and  $^\bullet\text{PrOH}$  radicals. We found no evidence for putative dihydropyridine  $\text{PyH}_2^{35}$  or a hydrogen-bonded Py dimer  $\text{PyH}^+\cdots\text{Py}$ ,<sup>36</sup> which should have appeared as  $m/z^+ = 82$  and 159, respectively. More generally, most of the myriad products observed in the mass spectra can be accounted for from radical addition and disproportionation reactions among [ $1\text{-PyH}^\bullet$ ,  $^\bullet\text{PrOH}$ ] primary and secondary radicals. For example, positive  $m/z^+ = 200$  is the protonated form of the 199 Da mass neutrals resulting from  $^\bullet\text{PrOH}$  addition to mass 139 Da above, followed by a radical disproportionation that incorporates an additional H atom, that is,  $199 = 139 + 59 +$



**Figure 2.** (A)  $\text{MS}^2$  of  $m/z^+ = 98$ ; (B)  $\text{MS}^2$  of  $m/z^+ = 116$ ; (C)  $\text{MS}^2$  of  $m/z^+ = 158$ ; (D)  $\text{MS}^2$  of  $m/z^+ = 200$ . Note the neutral 18 ( $\text{H}_2\text{O}$ ), 58 ( $\text{CO}(\text{CH}_3)_2$ ), and 60 Da (2-PrOH) losses.

1. Similarly,  $m/z^+ = 196$  is the protonated form of  $195 = \text{Py} + 2^\bullet\text{PrOH} - 2\text{H} = 79 + 118 - 2$ , that is, the result of successive additions of  $^\bullet\text{PrOH}$  followed by H atom losses via disproportionation and so forth.

More relevant to the title issue is the appearance of even mass negative ions as products of the photolysis of Py in 2-PrOH/ $\text{H}_2\text{O}$  containing dissolved  $\text{CO}_2$ . This is so because the addition of  $1\text{-PyH}^\bullet$  to  $\text{CO}_2$  would give rise to a 124 Da radical preserving the O–C–O moiety, which should end up as a 125 Da =  $80$  ( $1\text{-PyH}^\bullet$ ) +  $44$  ( $\text{CO}_2$ ) +  $1$  (H) carbamic acid that will appear at  $m/z^- = 124$ . Following this search criterion, we found that the only even mass negative ion peaks whose intensities increased significantly in photolysis experiments performed in the presence of  $\text{CO}_2$  were those at  $m/z^- = 124$  and  $160 = 124 + 36$  ( $2\text{H}_2\text{O}$ ) (Figure 3 and Scheme 1). We noticed the same behavior also in the odd  $m/z^- = 113$  anion, which we ascribe to  $(\text{HCOO})_2\text{Na}^-$ . Confirming our structural assignments, we found that these three anions contain carboxylate groups that split 44 Da  $\text{CO}_2$  neutrals via collisionally induced dissociation (Figure 4). These species represent evidence of a process triggered by the photoexcitation of Py in 2-PrOH, reaction R1, followed by reaction R2

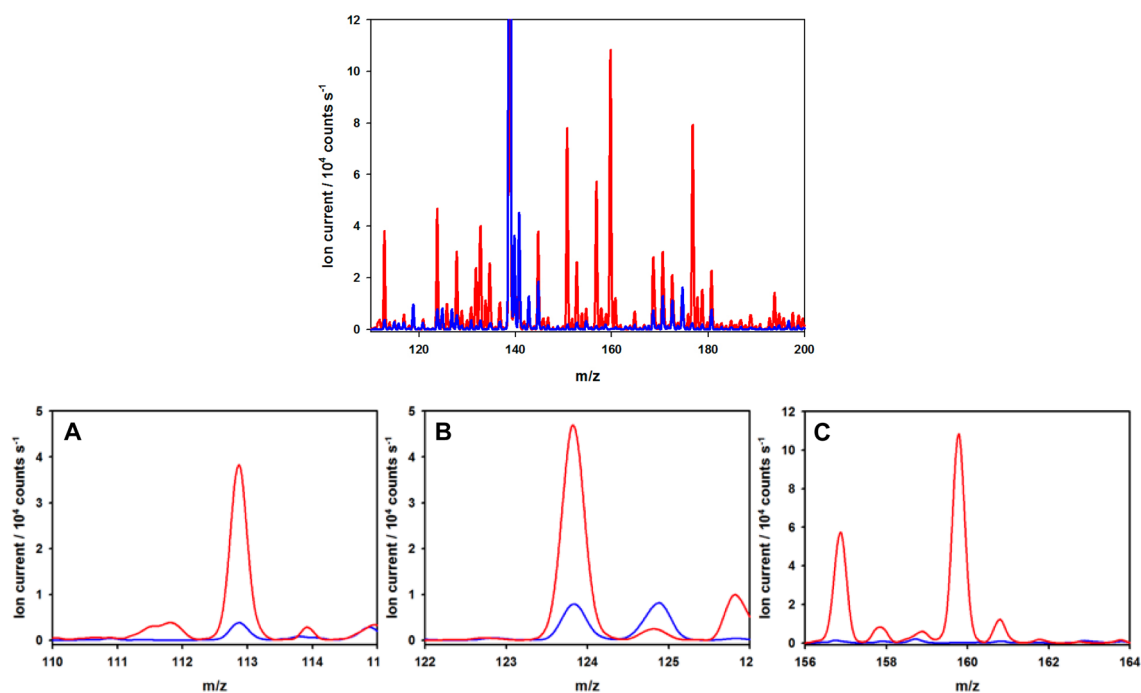


and subsequent reactions of  $^\bullet\text{Py-1-COOH}$  toward the observed products (Scheme 1).

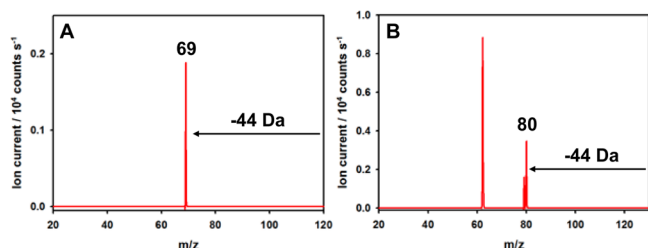
An order of magnitude (O) estimate of the rate constant  $k_2$  at which  $1\text{-PyH}^\bullet$  adds to  $\text{CO}_2$  may be obtained by assuming that reaction R2 competes with the faster radical termination reactions, reaction R3



where  $\text{X}^\bullet$  is any of the radicals formed in this system. From the reported photon output of our lamp,<sup>27</sup>  $F = 3 \times 10^{15}$  photons/s =  $5 \times 10^{-9}$  mol/s, which is fully absorbed by  $[\text{Py}] > 1$  mM solutions (see above), we derive an upper limit to free radical initiation rates in our system,  $R_i \leq 5 \times 10^{-7} \text{ M s}^{-1}$ . Hence, with a typical value of diffusionally controlled radical recombination rate constant,  $k_3 \approx 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , we obtain an upper limit for steady-state radical concentrations,  $[1\text{-PyH}^\bullet]_{\text{ss}} \leq 1 \times 10^{-8} \text{ M}$ . By making the reasonable assumption that the overall quantum yield of the products resulting from the addition of 1-



**Figure 3.** Negative ion ESI mass spectra. (Blue trace) 10 mM Py in 10% (v/v) 2-PrOH/H<sub>2</sub>O irradiated at 254 nm for 1 h. (Red trace) 10 mM Py in 10% (v/v) 2-PrOH/H<sub>2</sub>O saturated with CO<sub>2</sub> irradiated at 254 nm for 1 h. (A–C) Zoom into the mass ranges where the  $m/z^- = 113$ , 124, and 160 products appear, respectively.



**Figure 4.** (A) MS<sup>2</sup> of  $m/z^- = 113$ ; (B) MS<sup>2</sup> of  $m/z^- = 124$ . Note the neutral 44 (CO<sub>2</sub>) Da losses.

PyH• + CO<sub>2</sub> is small,  $\phi_{\text{CO}_2} \approx 0.01\text{--}0.1$  (i.e., that reaction R2 may be neglected as a first approximation into the overall radical mass balance), we get eq E1

$$\phi 2k_3[1\text{-PyH}^\bullet]_{\text{ss}}^2 \approx k_2[1\text{-PyH}^\bullet]_{\text{ss}}[\text{CO}_2] \quad (\text{E1})$$

and from  $[\text{CO}_2] = 3.5 \times 10^{-2}$  M (saturated under 1 atm of CO<sub>2</sub>), we derive  $k_2/\phi \leq 570 \text{ M}^{-1} \text{ s}^{-1}$ . In other words, we estimate that  $k_2 \approx O(10) \text{ M}^{-1} \text{ s}^{-1}$  under the present conditions. Hence, from  $k_2 = A_2 \exp(-E_2/RT)$  and a typical value for the A factor of a polyatomic 1-PyH• radical addition to linear CO<sub>2</sub>,  $A_2 \approx 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>37</sup> we infer that  $E_2 \geq 9 \text{ kcal mol}^{-1}$  for reaction R2 in water. We note that this value is a few kcal mol<sup>-1</sup> smaller than, but certainly compatible with, an estimated 13.6–16.5 kcal mol<sup>-1</sup> energy barrier for the addition of 1-PyH• to CO<sub>2</sub> in water clusters.<sup>18,25</sup>

Next, we deemed it important to check whether the detection of products ascribable to the 2e<sup>-</sup> reduction of CO<sub>2</sub> and the range of estimated kinetic parameters derived from our experiments are at least compatible with recent thermochemical estimates for reaction R2. Estimated values for enthalpies of formation and dissociation energies of relevant gas-phase species at 298 K are given in Table 1. Here, we assume that because the enthalpies of hydration of these neutral species are

**Table 1. Thermodynamic Data for Gas-Phase Species at 298 K**

species	$\Delta H_f^\circ$ D in kcal mol <sup>-1</sup>
CO <sub>2</sub>	−94 <sup>46</sup>
Py	33
D[•C(Me) <sub>2</sub> O–H]	25 <sup>47</sup>
1-PyH•	<60 <sup>a</sup> , 56 <sup>22</sup>
pyridine-1(H)-carboxylic acid (HPy-1-COOH)	−61 <sup>b</sup>
4-pyridinyl-1(H)-carboxylic acid (•Py-1-COOH)	−36 <sup>c</sup>

<sup>a</sup>From  $D[1\text{-Py–H}^\bullet] > D[\bullet\text{C}(\text{Me})_2\text{O–H}]$ .<sup>32,38</sup> <sup>b</sup>From group additivity.<sup>39</sup> <sup>c</sup>Considers that the dissociation of the C–H bond in H–Py-1-COOH gives rise to a diallylic •Py-1-COOH radical, that is,  $D[\text{H–Py-1-COOH}] \approx 77 \text{ kcal mol}^{-1}$ .<sup>40,41</sup>

small, they will nearly compensate for each other and, therefore, that our semiquantitative arguments should apply in aqueous solutions. Because •PrOH can reduce Py by transferring a H atom,<sup>38</sup> we infer that the dissociation energy of the N–H bond in 1-Py–H• is stronger than the O–H bond in [•C(Me)<sub>2</sub>O–H], that is:  $D[1\text{-Py–H}^\bullet] > D[\bullet\text{C}(\text{Me})_2\text{O–H}] = 25 \text{ kcal mol}^{-1}$  (see Table 1). We note that this lower bound is in agreement with the  $D[1\text{-Py–H}^\bullet] \approx 30 \text{ kcal mol}^{-1}$  value obtained from recent quantum mechanical calculations.<sup>22</sup> These  $D[1\text{-Py–H}^\bullet]$  values lead to  $60 > \Delta H_f^\circ[1\text{-Py–H}^\bullet] > 56 \text{ kcal mol}^{-1}$  values for the enthalpy of formation of 1-Py–H•. The required enthalpy of formation of •Py-1-COOH, the product of reaction R2, can be estimated from that of the parent dihydropyridine carboxylic acid,  $\Delta H_f^\circ[\text{HPy-1-COOH}] = -61 \text{ kcal mol}^{-1}$ , obtained from group additivity<sup>39</sup> by assuming that the dissociation of the C–H bond in H–Py-1-COOH generates a diallylic 3-pentadienyl radical, that is,  $D[\text{H–Py-1-COOH}] \approx 77 \text{ kcal mol}^{-1}$ .<sup>40,41</sup> Thus, from the data of Table 1, we estimate  $\Delta H_r^\circ(\text{R2}) = [-36 - (-94) - 56] = +2 \text{ kcal mol}^{-1}$  within a few kcal mol<sup>-1</sup>, which is commensurate but somewhat smaller, as it should be, than the



$E_2 \geq 9 \text{ kcal mol}^{-1}$  value that we derived from our experiments and the lower bound of  $\geq 14 \text{ kcal mol}^{-1}$  reported by Musgrave et al. for  $E_2$  in water clusters.<sup>25</sup> In other words, we envision that  $\bullet\text{Py-1-COOH}$ , the neutral product of reaction R2, is a marginally stable radical species that could readily revert to the reactants but will be stabilized as  $\bullet\text{Py-1-COO}^-$  by releasing a proton and thereby becoming hydrated or as a closed-shell species via H-abstraction by disproportionating with  $\bullet\text{PrO-H}$ .

The reasons why  $1\text{-PyH}^\bullet$  is singularly able to add to  $\text{CO}_2$  along a relatively accessible reaction pathway at room temperature have been presented before. ESR studies have indicated that most of the unpaired spin in  $1\text{-PyH}^\bullet$  is localized on the N atom.<sup>42–45</sup> Thus, reaction R2, which amounts to a H atom transfer, may in fact proceed via the partial transfer of the unpaired spin density localized on the N atom into the antibonding LUMO of  $\text{CO}_2$ , followed by intramolecular proton transfer.<sup>25</sup> The subsequent ionization of the marginally stable  $\bullet\text{Py-1-COOH}$  adduct (which otherwise would have a fleeting existence; see above) into  $1\text{-PyCOO}^\bullet$  is mediated by surrounding water molecules and plays a crucial role in lowering the apparent activation barrier for reaction R2. In  $1\text{-PyCOO}^\bullet$ , the Py ring regains its aromaticity, while  $\text{CO}_2$  is halfway reduced to formate.

In summary, we have obtained, apparently for the first time, experimental evidence that  $1\text{-H-pyridinyl}$  does react with  $\text{CO}_2$ , homogeneously, in water, en route to products derived from what amounts to a  $2e^-$  reduction process.

## AUTHOR INFORMATION

### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Lackner, K. S. Capture of Carbon Dioxide from Ambient Air. *Eur. Phys. J.: Spec. Top.* **2009**, *176*, 93–106.
- (2) Wang, T.; Lackner, K. S.; Wright, A. Moisture Swing Sorbent for Carbon Dioxide Capture from Ambient Air. *Environ. Sci. Technol.* **2011**, *45*, 6670–6675.
- (3) Olah, G. A.; Prakash, G. K. S.; Goepfert, A. Anthropogenic Chemical Carbon Cycle for a Sustainable Future. *J. Am. Chem. Soc.* **2011**, *133*, 12881–12898.
- (4) Stauffer, P. H.; Keating, G. N.; Middleton, R. S.; Viswanathan, H. S.; Berchtod, K. A.; Singh, R. P.; Pawar, R. J.; Mancino, A. Greening Coal: Breakthroughs and Challenges in Carbon Capture and Storage. *Environ. Sci. Technol.* **2011**, *45*, 8597–8604.
- (5) Liu, X.; Du, P. W.; Cao, R. Trinuclear Zinc Complexes for Biologically Relevant  $\mu_3$ -Oxoanion Binding and Carbon Dioxide Fixation. *Nat. Commun.* **2013**, *4*, 2375.
- (6) Quinn, R. Ion Exchange Resins as Reversible Acid Gas Absorbents. *Sep. Sci. Technol.* **2003**, *38*, 3385–3407.
- (7) Marshall, J. Solar Energy: Springtime for the Artificial Leaf. *Nature* **2014**, *510*, 22–24.
- (8) Faunce, T.; Styring, S.; Wasielewski, M. R.; Brudvig, G. W.; Rutherford, A. W.; Messinger, J.; Lee, A. F.; Hill, C. L.; deGroot, H.; Fontecave, M.; et al. Artificial Photosynthesis as a Frontier Technology for Energy Sustainability. *Energy Environ. Sci.* **2013**, *6*, 1074–1076.
- (9) Faunce, T. A.; Lubitz, W.; Rutherford, A. W.; MacFarlane, D. R.; Moore, G. F.; Yang, P. D.; Nocera, D. G.; Moore, T. A.; Gregory, D. H.; Fukuzumi, S.; et al. Energy and Environment Policy Case for a Global Project on Artificial Photosynthesis. *Energy Environ. Sci.* **2013**, *6*, 695–698.
- (10) Tu, W. G.; Zhou, Y.; Zou, Z. G. Photocatalytic Conversion of  $\text{CO}_2$  into Renewable Hydrocarbon Fuels: State-of-the-Art Accomplishment, Challenges, and Prospects. *Adv. Mater.* **2014**, *26*, 4607–4626.
- (11) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; et al. Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of  $\text{CO}_2$  Fixation. *Chem. Rev.* **2013**, *113*, 6621–6658.
- (12) Kondratenko, E. V.; Mul, G.; Baltrusaitis, J.; Larrazabal, G. O.; Perez-Ramirez, J. Status and Perspectives of  $\text{CO}_2$  Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes. *Energy Environ. Sci.* **2013**, *6*, 3112–3135.
- (13) Kumar, B.; Llorente, M.; Froehlich, J.; Dang, T.; Sathrum, A.; Kubiak, C. P. Photochemical and Photoelectrochemical Reduction of  $\text{CO}_2$ . *Annu. Rev. Phys. Chem.* **2012**, *63*, 541.
- (14) Mikkelsen, M.; Jorgensen, M.; Krebs, F. C. The Teraton Challenge. A Review of Fixation and Transformation of Carbon Dioxide. *Energy Environ. Sci.* **2010**, *3*, 43–81.
- (15) Olson, J. M. Evolution of Photosynthesis. *Science* **1970**, *168*, 438.
- (16) Gutsev, G. L.; Bartlett, R. J.; Compton, R. N. Electron Affinities of  $\text{CO}_2$ , OCs, and  $\text{Cs}_2$ . *J. Chem. Phys.* **1998**, *108*, 6756–6762.
- (17) Jitaru, M.; Lowy, D. A.; Toma, M.; Toma, B. C.; Oniciu, L. Electrochemical Reduction of Carbon Dioxide on Flat Metallic Cathodes. *J. Appl. Electrochem.* **1997**, *27*, 875–889.
- (18) Morris, A. J.; McGibbon, R. T.; Bocarsly, A. B. Electrocatalytic Carbon Dioxide Activation: The Rate-Determining Step of Pyridinium-Catalyzed  $\text{CO}_2$  Reduction. *ChemSusChem* **2011**, *4*, 191–196.
- (19) Seshadri, G.; Lin, C.; Bocarsly, A. B. A New Homogeneous Electrocatalyst for the Reduction of Carbon-Dioxide to Methanol at Low Overpotential. *J. Electroanal. Chem.* **1994**, *372*, 145–150.
- (20) Cercek, B.; Ebert, M. Pulse Radiolysis Studies of Reaction of H and OH Radicals and Hydrated Electrons with Pyridine. *Trans. Faraday Soc.* **1967**, *63*, 1687.
- (21) Fessende, R.; Neta, P. ESR-Spectra of Radicals Produced by Reduction of Pyridine and Pyrazine. *Chem. Phys. Lett.* **1973**, *18*, 14–17.
- (22) Golec, B.; Das, P.; Bahou, M.; Lee, Y. P. Infrared Spectra of the  $1\text{-Pyridinium}$  ( $\text{C}_5\text{H}_5\text{NH}^+$ ) Cation and Pyridinyl ( $\text{C}_5\text{H}_5\text{NH}$  and  $4\text{-C}_5\text{H}_6\text{N}$ ) Radicals Isolated in Solid *para*-Hydrogen. *J. Phys. Chem. A* **2013**, *117*, 13680–13690.
- (23) Keith, J. A.; Carter, E. A. Theoretical Insights into Pyridinium-Based Photoelectrocatalytic Reduction of  $\text{CO}_2$ . *J. Am. Chem. Soc.* **2012**, *134*, 7580–7583.
- (24) Keith, J. A.; Carter, E. A. Electrochemical Reactivities of Pyridinium in Solution: Consequences for  $\text{CO}_2$  Reduction Mechanisms. *Chem. Sci.* **2013**, *4*, 1490–1496.
- (25) Lim, C. H.; Holder, A. M.; Musgrave, C. B. Mechanism of Homogeneous Reduction of  $\text{CO}_2$  by Pyridine: Proton Relay in Aqueous Solvent and Aromatic Stabilization. *J. Am. Chem. Soc.* **2013**, *135*, 142–154.
- (26) Ertem, M. Z.; Konezny, S. J.; Araujo, C. M.; Batista, V. S. Functional Role of Pyridinium During Aqueous Electrochemical Reduction of  $\text{CO}_2$  on Pt(111). *J. Phys. Chem. Lett.* **2013**, *4*, 745–748.
- (27) Johnson, P. V.; Hodyss, R.; Chernow, V. F.; Lipscomb, D. M.; Goguen, J. D. Ultraviolet Photolysis of Amino Acids on the Surface of Icy Solar System Bodies. *Icarus* **2012**, *221*, 800–805.
- (28) Enami, S.; Mishra, H.; Hoffmann, M. R.; Colussi, A. J. Hofmeister Effects in Micromolar Electrolyte Solutions. *J. Chem. Phys.* **2012**, *136*, 154707.
- (29) Enami, S.; Sakamoto, Y.; Colussi, A. J. Fenton Chemistry at Aqueous Interfaces. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 623–628.
- (30) Wilzbach, K. E.; Rausch, D. J. Photochemistry of Nitrogen Heterocycles. Dewar Pyridine and Its Intermediacy in Photoreduction

and Photohydration of Pyridine. *J. Am. Chem. Soc.* **1970**, *92*, 2178–2179.

(31) Kaplan, L.; Wilzbach, K. E.; Pavlik, J. W. Photohydration of Pyridinium Ions. *J. Am. Chem. Soc.* **1972**, *94*, 3283.

(32) Zeldes, H.; Livingston, R. Paramagnetic-Resonance Study of Liquids During Photolysis. 14. Pyridine, Pyrazine, Pyrimidine, and Pyridazine. *J. Phys. Chem.* **1972**, *76*, 3348.

(33) Zeldes, H.; Livingston, R. Electron-Spin Resonance Study of Radicals Produced by One-Electron Reduction of Nicotinic-Acid, Nicotinamide, and Methyl Nicotinate. *J. Magn. Reson.* **1977**, *26*, 103–108.

(34) Terokubota, S.; Akiyama, K.; Ikoma, T.; Ikegami, Y. Time-Resolved EPR Studies on the Photochemical Hydrogen Abstraction Reactions and the Excited Triplet-States of 4-Substituted Pyridines. *J. Phys. Chem.* **1991**, *95*, 766–770.

(35) Keith, J. A.; Carter, E. A. Theoretical Insights into Electrochemical CO<sub>2</sub> Reduction Mechanisms Catalyzed by Surface-Bound Nitrogen Heterocycles. *J. Phys. Chem. Lett.* **2013**, *4*, 4058–4063.

(36) Yan, Y.; Gu, J.; Bocarsly, A. B. Hydrogen Bonded Pyridine Dimer: A Possible Intermediate in the Electrocatalytic Reduction of Carbon Dioxide to Methanol. *Aerosol Air Qual. Res.* **2014**, *14*, 515–521.

(37) Abel, B.; Assmann, J.; Buback, M.; Grimm, C.; Kling, M.; Schmatz, S.; Schroeder, J.; Witte, T. Ultrafast Decarboxylation of Carbonyloxy Radicals: Influence of Molecular Structure. *J. Phys. Chem. A* **2003**, *107*, 9499–9510.

(38) Neta, P. Electron-Spin Resonance Study of Radicals Produced by One-Electron Reduction of Pyridines. *Radiat. Res.* **1972**, *52*, 471–480.

(39) Joback, K. G.; Reid, R. C. Estimation of Pure-Component Properties from Group-Contributions. *Chem. Eng. Commun.* **1987**, *57*, 233–243.

(40) Agapito, F.; Nunes, P. M.; Cabral, B. J. C.; dos Santos, R. M. B.; Simoes, J. A. M. Energetics of the Allyl Group. *J. Org. Chem.* **2007**, *72*, 8770–8779.

(41) Clark, K. B.; Culshaw, P. N.; Griller, D.; Lossing, F. P.; Simoes, J. A. M.; Walton, J. C. Studies of the Formation and Stability of Pentadienyl and 3-Substituted Pentadienyl Radicals. *J. Org. Chem.* **1991**, *56*, 5535–5539.

(42) Dohrmann, J. K.; Kieslich, W. Electron-Spin Resonance Study of 1-Hydropyridinyl Radicals in Solution — 4-Acetylpyridine and Pyridine-4-Carbaldehyde. *J. Magn. Reson.* **1978**, *31*, 69–74.

(43) Neta, P.; Patterson, L. K. Substituted Pyridinyl Radicals in Aqueous-Solutions. Formation, Reactivity, and Acid–Base Equilibria. *J. Phys. Chem.* **1974**, *78*, 2211–2217.

(44) Bower, H. J.; McRae, J. A.; Symons, M. C. R. Unstable Intermediates. 53. An Electron Spin Resonance Study of Radical Formed by Addition of a Hydrogen Atom to Pyridinium Ion. *J. Chem. Soc. A* **1968**, 1918.

(45) Rhodes, C. J.; Morris, H.; Reid, I. D. Muonium Atom Addition to Pyridine and to the Pyridinium Cation. *Magn. Reson. Chem.* **2001**, *39*, 438–442.

(46) NIST Standard Reference Database Number 69; National Institute of Standards and Technology: Gaithersburg, MD, 2011.

(47) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.