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Electrochemistry of Acids on Platinum. Application to the Reduction of Carbon Dioxide in the Presence of Pyridinium Ion in Water

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S *Supporting Information*

ABSTRACT: A detailed cyclic voltammetric investigation of the reduction of moderately weak acids on platinum reveals that they are reduced in two steps: one involving the hydrated protons initially present at equilibrium and the second the reduction of the acid through its prior conversion into hydrated protons. The reduction of pyridinium ions (protonated pyridine) follows this reaction scheme as does any other acid of similar pK (e.g., acetic acid). Rather than being catalytically reduced, CO_2 plays a similar role through its prior conversion to carbonic acid. No trace of methanol or formate could be detected upon preparative-scale electrolysis of CO_2 on the same electrode in the presence of pyridinium ions.

The electrochemical reduction of hydrated proton on platinum electrodes has the reputation of being one of the most studied electrode reactions.[1,2] In spite of this, we have found features of the reduction of moderately weak acids on platinum in aqueous solutions that have not been uncovered so far. Our interest in the matter was aroused by the report that carbon dioxide can be reduced to methanol on a platinum electrode in aqueous solutions containing pyridinium ions (PyH^+). Faradaic yields up to 20% were reported,[3,4] a quite interesting result in the framework of the contemporary efforts to convert CO_2 into fuels.[5] The interpretation of this intriguing result was that the pyridinium ion works as a homogeneous catalyst through its reduction to the pyridinium radical, $PyH^\bullet$, that would then react with CO_2, ultimately leading to methanol after a series of follow-up steps. A rate constant for the key step, in which an adduct is formed by combination of $PyH^\bullet$ with CO_2, was derived from the cyclic voltammetry (CV) of PyH^+ in the presence of CO_2.[3,4] This report has triggered several quantum computational contributions leading to divergent conclusions as to the likelihood of the proposed mechanism.[4,6−10] In spite of the simple evidence provided by the fact that no reduction wave is observed in the CV of PyH^+ on an inert electrode such as glassy carbon,[11] only the last of these computational contributions[10] takes into account the participation of platinum atoms to the catalytic reaction.

We were puzzled by several aspects of the proposed mechanism: (i) How can a reaction pathway counting for only 20% of the overall reduction process be responsible for 100% of the characteristics of the cyclic voltammetric responses? (ii) The features of the cyclic voltammetric reduction wave, deemed catalytic, are not actually what one would expect for a typical catalytic wave where the replacement of the peak by a plateau is accompanied by a large increase of the current.[12] Confusion arises in this connection by the fact that the S-shape was reported to appear only at very low scan rates (0.001 V/s). In these conditions, natural convection heavily interferes, besides diffusion, giving rise also to S-shaped cyclic voltammetric responses even in the absence of catalysis.[13]

We thus re-examined the question starting with the CV of PyH^+ alone on a polycrystalline platinum disk electrode. Besides the chemical and electrochemical reversibility, or quasi-reversibility, the most striking feature of the ensuing CV responses is the appearance of two waves ~2 pH units below the PyH^+ pK (Figure1). The first of these waves increases upon decreasing the pH and vice versa. One expects such moderately weak acids to give rise to a "CE" mechanism[16] in which the reduction goes through the reduction of the hydrated proton, which is rapidly regenerated as soon as reduced from the dissociation of the acid in view of the well-known rapidity of proton transfer from nitrogen and oxygen acids in water. This is indeed what has been observed at the occasion of an exhaustive study with dimethylsulfoxide as the solvent.[17] As the pH is decreased below the PyH^+ (or AcOH) pK, the concentration of hydrated protons at equilibrium tends to become larger than the PyH^+ concentration, as represented in Figure 2 concomitantly with the splitting of the wave and the increase of the newly appeared wave. One is thus led to assign this new wave to the direct reduction of hydrated protons. That the current corresponding to this reduction reaches a peak, being then controlled by hydrated proton diffusion, may seem surprising in view of the well-known rapidity of proton transfer in nitrogen and oxygen acids evoked earlier. However as seen in Figure 2, in the pH zone where the first wave develops, the concentration of acid does not vary significantly. Significant displacement of the acid dissociation equilibrium to regenerate hydrated proton takes place once hydrated proton concentration close to the electrode is small. Consequently, the second wave corresponding to acid reduction through the reduction of the hydrated proton develops once hydrated protons initially present in solution have been reduced at the level of the first wave. The above mechanism in which the first wave corresponds to the direct reduction of hydrated protons and the second to the reduction of the hydrated protons generated by the rapid dissociation of the acid is confirmed by the simulations shown in Figure 1[18] according to the mechanism

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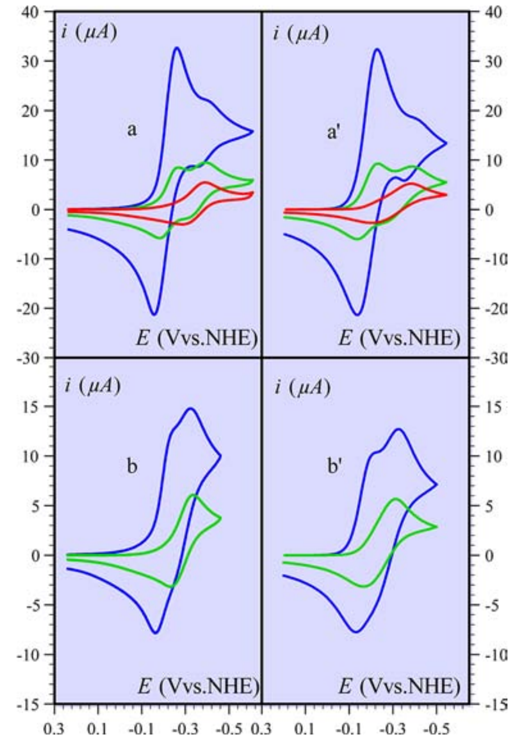


Figure 1. CV of a 2 mM solution of pyridine (a,a′) and 3 mM or 2 mM of acetic acid (b,b′) on a platinum electrode at 0.2 V/s in presence of 0.1 M KNO_3, T = 295 K, as a function of pH: a,a′: 2.5 (blue), 3 (green), 4 (red). b,b′: 3 (blue), 4 (green). a,b: experimental, a′,b′: simulated with pK_{PyH^+} = 5.2 and pK_{AcOH} = 4.75,[14] $E^{0,ap}_{H^+/1/2H_2}$ = −0.15 V vs NHE, $k^{S,ap}_{H^+/1/2H_2}$ = 0.03 cm s^{-1}, α_{ap} = 0.7. Diffusion coefficients (10^{-5} cm^2 s^{-1}): D_{H^+} = 9.3, D_{H_2} = 5, D_{PyH^+} = 1, D_{Pyr} = 0.6, D_{AcO^-} = 1.1, D_{AcOH} = 1.3.[15]

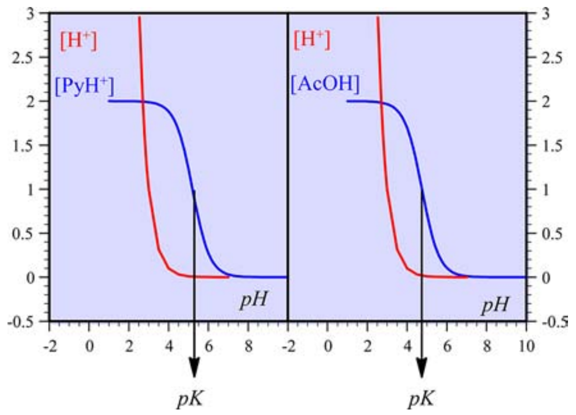
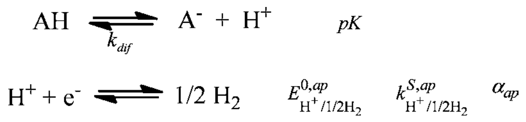


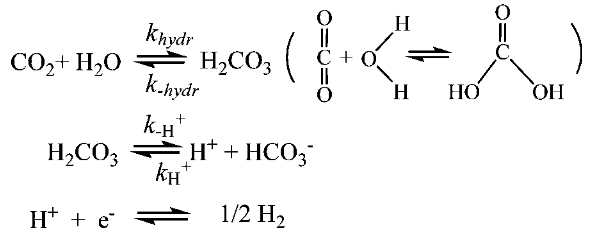
Figure 2. Equilibrium concentrations of hydrated protons and acid (in mM) in a 2 mM pyridine and acetic acid solutions as a function of pH. pKs are respectively 5.2 and 4.75.

Scheme 1. AH Reduction Mechanism (AH = $PyrH^+$ or AcOH)



sketched in Scheme 1 and taking into account the apparent kinetics of hydrated proton reduction on platinum.

Scheme 2



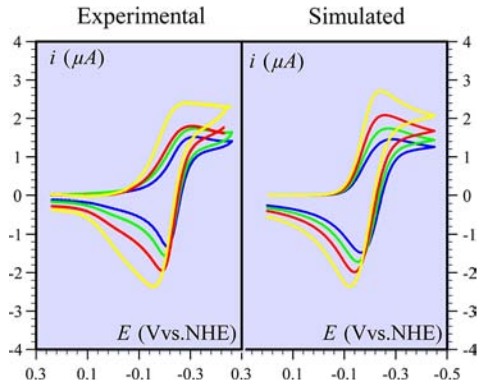


Figure 3. CV of a CO_2 saturated solution at pH = 3.9 on a platinum electrode in presence of 0.1 M KNO_3, T = 295 K, as a function of the scan rate (V/s): 0.05 (blue), 0.1 (green), 0.2 (red), 0.5 (yellow). Diffusion coefficients (10^{-5} cm^2 s^{-1}): D_{H^+} = 9.3, D_{H_2} = 5, D_{CO_2} = 1.5, $D_{H_2CO_3} \approx D_{HCO_3^-}$ = 1.2.[15] $E^{0,ap}_{H^+/1/2H_2}$ = −0.15 V vs NHE, $k^{S,ap}_{H^+/1/2H_2}$ = 0.03 cm s^{-1}, α_{ap} = 0.7. [CO_2] = 0.0383 M. $k_{hydr}/k_{-hydr} = K_{hydr} = 1.7 \times 10^{-3}$; $k_{hydr} = 3 \times 10^{-2}$ s^{-1}. $k_{-H^+}/k_{H^+} = 10^{-3.6}$; $k_{H^+} = 10^{10}$ M^{-1} s^{-1}.

Indeed, although close to electrochemical reversibility, simulation does require correctly taking into account the reduction mechanism and its kinetic characteristics, as summarized in the caption of Figure 1. For the sake of simplicity, we assume here that the H^+/H_2 electrochemical reaction can be described by an apparent Butler−Volmer kinetics which characteristics are $E^{0,ap}_{H^+/1/2H_2}$, $k^{S,ap}_{H^+/1/2H_2}$, and α_{ap} (apparent standard potential, standard rate constant, and transfer coefficient, respectively) obtained from a fitting of the cyclic voltammograms obtained with the direct reduction of hydrated proton on the same platinum electrode (see Supporting Information). Since a nitrogen or oxygen acid is dealt with, proton transfer could be assumed to be fast enough to remain at equilibrium. Besides this CE pathway involving a fast deprotonation step prior to electron transfer to H^+, we cannot exclude the occurrence of another reaction path in which these two events would be concerted. To the best of our knowledge, this is the first observation and explanation of a two-stage reduction on platinum of a weak acid in water, which involves the reduction of hydrated proton at each stage.

Focusing on the reduction of PyH^+ on platinum in the pH range of interest, we are thus led to conclude that it does not produce the $PyH^\bullet$ radical but consists in the reduction of the hydrated protons generated by the rapid dissociation of the PyH^+ ions. The situation is in fact quite similar to what happens with another acid of closely similar pK, acetic acid (pK = 4.75) as seen upon perusal of Figures 1 and 2.

We now turn to the reduction of CO_2 on platinum in the absence of PyH^+ or of any other acid. Hydrated CO_2 indeed behaves as a Brönsted acid through its conversion into H_2CO_3

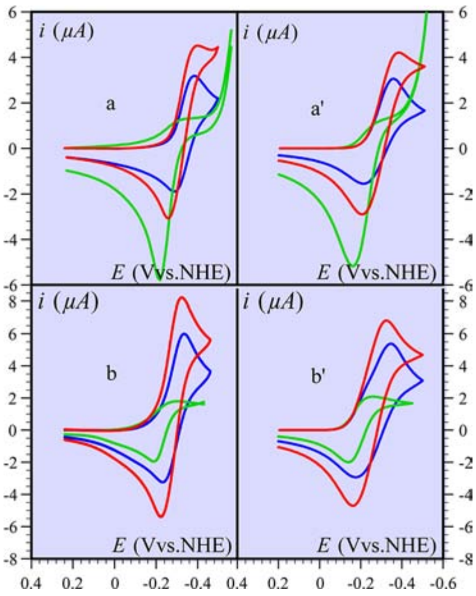


Figure 4. CV of a CO_2-saturated solution of 3 mM pyridine (a,a′) and 3 mM acetic acid (b,b′) on a platinum electrode in presence of 0.1 M KNO_3, $T = 295$ K, at pH = 5.15 (a,a′) and 4 (b,b′). Scan rate: 0.1 V/s (a,a′) and 0.2 V/s (b,b′). blue: acid alone; green: CO_2 alone (pH = 4.5 in a,a′ and 4 in b,b′); red: acid + CO_2. a,b: experimental; a′,b′: simulations. Simulation parameters: Diffusion coefficients (10^{-5} cm^2 s^{-1}): $D_{H^+} = 9.3$, $D_{H_2} = 5$, $D_{PyH^+} = 1$, $D_{Pyr} = 0.6$, $D_{AcO^-} = 1.1$, $D_{AcOH} = 1.3$, $D_{CO_2} = 1.5$, $D_{H_2CO_3} = D_{HCO_3^-} = 1.2$. $E^{0,ap}_{H^+/1/2H_2} = -0.15$ V vs NHE, $k^{S,ap}_{H^+/1/2H_2} = 0.03$ cm s^{-1}, $\alpha_{ap} = 0.7$. $[CO_2] = 0.0383$ M. $k_{hydr}/k_{-hydr} = K_{hydr} = 1.7 \times 10^{-3}$; $k_{hydr} = 3 \times 10^{-2}$ s^{-1}. $k_{-H}{}^{+}/\ k_{H}{}^{+} = 10^{-3.6}$; $k_{H}{}^{+} = 10^{10}$ M^{-1} s^{-1}. Protonation rate constants for Pyr and AcO^-: 10^{10} M^{-1} s^{-1}.

as sketched in Scheme 2. Figure 3 summarizes experiments carried out with a CO_2 saturated solution at pH 3.9, varying the scan rate. As compared to the other acids, there is a clear tendency to obtain a S-shaped wave, which plateau current is much smaller than expected for complete CO_2 reduction at the electrode surface due to the large CO_2 concentration in CO_2 saturated water (0.0383 M).[19]

These particular features indicate that the generation of the hydrated proton from CO_2 is slower than it was with the previous acids. This is not really surprising since CO_2 has to be hydrated before the resulting carbonic acid generates the hydrated protons. The latter reaction is expected to be very fast since it consists in a proton transfer from an oxygen acid as opposed to the CO_2 hydration step, which must overcome severe reorganization barriers caused by important changes of bond lengths and angles (see Scheme 2). Simulation of Scheme 2 reaction sequence, assuming that the proton transfer reaction remains at equilibrium (pK = 3.6),[19,20] with the same characteristics of the hydrated proton reduction as above, knowing that $k_{hydr}/k_{-hydr} = K_{hydr} = 1.7 \times 10^{-3}$,[19] leads to $k_{hydr} = 3 \times 10^{-2}$ s^{-1}, $k_{-hydr} = 17.65$ s^{-1}, in excellent agreement with literature data.[21]

We may now examine the cyclic voltammetric of CO_2 in the presence of PyH^+ and, for the sake of comparison, AcOH. It is seen (Figure 4) that at a pH where the reduction of hydrated proton does not occur directly but only through the "CE" pathway, the cyclic voltammetric responses involve simply the superposition of the contributions of the two acids present, PyH^+ or AcOH on the one hand and CO_2 on the other. There is again nothing special about PyH^+ that could involve the intermediary formation of $PyH^\bullet$ as shown by the simulation of the cyclic voltammetric responses and confirmed by the observation that AcOH behaves in a strictly similar manner. Upon scanning to more negative potentials, water itself is reduced (see green line in Figure 4a) leading also to formation of H_2 which is reoxidized on the reverse scan. This feature can be simulated (see green line in Figure 4a′) by considering an ad hoc Butler−Volmer kinetics for H_2O reduction.

In order to complement the cyclic voltammetric observations, we undertook detailed preparative-scale experiments following the indications of ref 22. The results are summarized in Table 1 (full details on the electrolysis instrumentation and procedures as well as on analysis of the electrolyzed solution are given in the SI). It is seen that, in spite of repeated efforts, neither methanol nor formate could be detected, besides an abundant production of dihydrogen (close to 100%), upon electrolysis of pyridinium CO_2 mixtures, with no detectable production of CO (see SI).

In summary, analysis of the CV of pyridinium or acetic acid solutions on platinum showed that the reduction solely involves hydrated protons. At pHs ~2 units below the pK, hydrated protons are reduced directly with no participation of the acid molecules. Upon raising the pH, a second wave appears at a more negative potential, which progressively replaces the first wave. It concerns again the reduction of hydrated protons, but this time the hydrated protons are generated by the rapid dissociation of the acid. The two acids behave quite similarly thus confirming the conclusion that the reduction of PyH^+ on platinum in the pH range of interest does not involve the $PyH^\bullet$ radical. CO_2 itself behaves in a similar manner through its hydration to carbonic acid, with the difference that the hydration reaction now interferes in the overall kinetics. The responses of mixtures of CO_2 with either pyridinium or acetic acid are simply the superposition of the contributions of the two components, showing again that the $PyH^\bullet$ radical does not transpire the reaction pathway. The results of repeated preparative-scale electrolyses on platinum in the presence of

Table 1. Preparative Scale Electrolyses[a]

regime	current density (μA/cm^2)	potential (V vs NHE)	$[PyrH^+]$(mM)	charge passed (coulombs)	faradaic yields methanol[b]	 formate[c]
galvanostatic	50	−0.55	10	243	≤0.3%	≤0.04%
potentiostatic	10	−0.46	10	40	≤2.2%	≤0.25%
	70	−0.56	4	60	≤1.5%	≤0.16%
	350	−0.76	4	300	≤0.3%	≤0.03%
	590	−0.96	4	800	≤0.1%	≤0.01%

[a] Under 1 atm CO_2; pH = 5.3; $[KNO_3] = 0.1$ M; volume electrolyzed =50 mL. [b] Estimated from the ability to detect $[MeOH] > 3 \times 10^{-5}$ M by NMR (see SI). [c] Estimated from the ability to detect $[HCO_2^-] > 10^{-5}$ M by ionic chromatography (see SI).

PyH^+ were surprisingly at variance with previously reported data since neither methanol nor formate could be detected besides an abundant production of dihydrogen.

Hydrogenated palladium electrodes seems to behave differently. The formation of substantial amounts of formate has been demonstrated on an electrode where palladium particles are dispersed within a polyviologen redox polymer under one atmosphere H_2.[23] More recently, the formation of methanol and formate on a hydrogenated palladium electrode has been reported.[3,22] In such cases, the hydride transfer from an electrogenerated palladium hydride to CO_2 may be invoked. If confirmed, the abundant formation of methanol upon electrolysis under illumination on a gallium phosphide electrode in the presence of PyH^+ [24] would call for a careful examination of actual role of this ingredient and of the chemical role of GaP.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, simulations for hydrated proton reduction.This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Vetter, K. J. *Electrochemical Kinetics*; Bruckensein, S., Howard, B., Trans. Eds.; Academic Press: New York, 1967; pp 516–614. (b) Bockris, J. O'M.; Ready, A. K. *Modern Electrochemistry*; Plenum Press: New York, 1983; Vol 2.

(2) Conway, B. E.; Tilak, B. V. *Electrochim. Acta* **2002**, *47*, 3571.

(3) Cole, E. B.; Lakkaraju, P. S.; Rampulla, D. M.; Morris, A. J.; Abelev, E.; Bocarsly, A. B. *J. Am. Chem. Soc.* **2010**, *132*, 11539.

(4) Morris, A. J.; McGibbon, R. T.; Bocarsly, A. B. *ChemSusChem* **2011**, *4*, 191.

(5) Costentin, C.; Robert, M.; Savéant, J.-M. *Chem. Soc. Rev.* **2013**, *42*, 2423.

(6) Tossell, J. A. *Comput. Theor. Chem.* **2011**, *977*, 123.

(7) Keith, J. A.; Carter, E. A. *J. Am. Chem. Soc.* **2012**, *134*, 7580.

(8) Lim, C.-H.; Holder, A. M.; Musgrave, C. B. *J. Am. Chem. Soc.* **2012**, *135*, 142.

(9) Keith, J. A.; Carter, E. A. *Chem. Sci.* **2013**, *4*, 1490.

(10) Ertem, M. Z.; Konezny, S. J.; Araujo, C. M.; Batista, V. S. *J. Phys. Chem. Lett.* **2013**, *4*, 745.

(11) As mentioned in ref 3 and verified by us.

(12) (a) Savéant, J.-M.; Vianello, E. In *Advances in Polarography*; 1st ed.; Longmuir, I. S., Ed.; Pergamon Press: Cambridge, U.K., 1959; Vol. *1*, p 367. (b) Savéant, J.-M. *Elements of molecular and biomolecular electrochemistry: an electrochemical approach to electron transfer chemistry*; John Wiley & Sons: Hoboken, NJ, 2006; chap. 2, section 2.2.6.

(13) Andrieux, C. P.; Hapiot, P.; Savéant, J.-M. *J. Electroanal. Chem.* **1993**, *349*, 299.

(14) *Handbook of Chemistry and Physics*, 81st ed.; CRC Press: Boca Raton, FL, 2000; pp 8–45.

(15) (a) *Handbook of Chemistry and Physics*, 81st ed.; CRC Press: Boca Raton, FL, 2000; pp 8–48. (b) For ions ref 15a pp 5–95 and 5–96. For AcOH and Pyridine: ref 15a pp 6–192. For H_2 and CO_2: ref 15a pp 6–191.

(16) (a) Savéant, J.-M.; Vianello, E. *Electrochim. Acta* **1962**, *8*, 905. (b) Ref 12b., chap. 2, pp. 92–94.

(17) Treimer, S. E.; Evans, D. H. *J. Electroanal. Chem.* **1998**, *449*, 39.

(18) Using DigiElch software. See: Rudolph, M. *J. Electroanal. Chem.* **2003**, *543*, 23.

(19) *Handbook of Chemistry and Physics*, 81st ed.; CRC Press: Boca Raton, FL, 2000; pp 8–90.

(20) *Handbook of Chemistry and Physics*, 81st ed.; CRC Press: Boca Raton, FL, 2000; pp 8–44.

(21) Ho, C.; Sturtevant, J. M. *J. Biol. Chem.* **1963**, *238*, 3499.

(22) Seshadri, G.; Lin, C.; Bocarsly, A. B. *J. Electroanal. Chem.* **1994**, *372*, 145.

(23) (a) Stalder, C. J.; Chao, S.; Summers, D. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 6318. (b) Stalder, C. J.; Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 3673.

(24) Barton, E. E.; Rampulla, D. M.; Bocarsly, A. B. *J. Am. Chem. Soc.* **2008**, *130*, 6342.