3982 J. Am. Chem. Soc. 1996, 118, 3982−3983

Homogeneous Catalysis of Electrochemical Hydrogen Evolution by Iron(0) Porphyrins

Iqbal Bhugun, Doris Lexa,[1] and Jean-Michel Savéant*

Laboratoire d'Electrochimie Moléculaire
de l'Université de Paris 7, Unité Associée au
CNRS No. 438, 2 Place Jussieu
75251 Paris Cedex 05, France

Received December 29, 1995

Catalysis of electrochemical hydrogen evolution from acidic solutions by various metal electrodes has attracted considerable and continuous attention.[2] Surprisingly, there are few examples of catalysis of the reaction by molecules dispersed in the solution or imbedded in a supporting phase coating the electrode surface. The only example of homogeneous catalysis by organic molecules involves pyridines and has been proposed to occur according to the following reaction scheme:[3]

$$\mathrm{Py} + \mathrm{AH} \rightleftharpoons \mathrm{PyH}^+ + \mathrm{A}^-, \quad 2\mathrm{PyH}^+ + 2e^- \rightarrow 2\mathrm{Py} + \mathrm{H}_2$$

There have also been relatively few attempts to use, as molecular catalysts, low-valent transition metal complexes, forming hydrides upon reaction with acids and evolving hydrogen heterolytically or homolytically. Heteropolytungstates (Si, P, Mo) electrodeposited on electrodes have been used successfully in this purpose.[4] Hydridocobaloxime has been shown to react, albeit slowly, with acids.[5] Co(I) porphyrins in solution, or attached to the electrode surface, catalyze hydrogen evolution in water.[6] However, the catalyst rapidly deactivates. Hydrogen evolution also occurs upon reaction of osmium and ruthenium porphyrin hydrides with acids. It involves the attack of the hydride by the acid.[7a] Several dihydrides of complexes containing two metal centers, designed to promote facile homolytic formation of hydrogen, do evolve hydrogen (see refs 7b,c and references therein).

We have found that iron porphyrins at the zero oxidation state ($PFe(0)^{2-}$), electrochemically generated from $PFe(III)^+$, PFe(II), $PFe(I)^-$ successively, are very efficient molecular catalysts of hydrogen evolution. Figure 1 shows the catalytic currents that are observed in cyclic voltammetry with iron tetraphenylporphyrin (TPP) in *N*,*N*′-dimethylformamide (DMF) in the presence of protonated triethylamine. In the absence of the acid, the iron porphyrin, introduced as TPPFeCl, exhibits three successive reversible one-electron waves corresponding to the successive formation of PFe(II), $PFe(I)^-$, and $PFe(0)^{2-}$.[8] Upon addition of the acid, the first two waves remain unchanged (this is shown in Figure 1 for wave 1/1′, representing the $Fe(II)/Fe(I)^-$ couple). The formation of $PFe(0)^{2-}$ at wave 2/2′ triggers the appearance of a catalytic irreversible wave, noted as 2C in Figure 1. We also note the presence at more negative potentials of a small but distinct reversible wave (3/3′). At low acid/catalyst concentration ratios, the catalytic wave occurs at a more positive potential than the $PFe(I)^-$, and $PFe(0)^{2-}$ couple which still gives rise to a reversible wave (Figure 1a). Upon raising the acid/catalyst concentration ratio, the catalytic wave increases in height and shifts in the negative direction thus merging with the 2/2′ wave while the reversibility disappears. This behavior is typical of a "total" catalysis situation where the catalytic reaction is so fast that the current is controlled by the diffusion of the substrate to the electrode surface.[9] Very similar results were obtained with CHF_2COOH as the acid, showing both the appearance of the catalytic wave 2C and the small wave 3/3′.

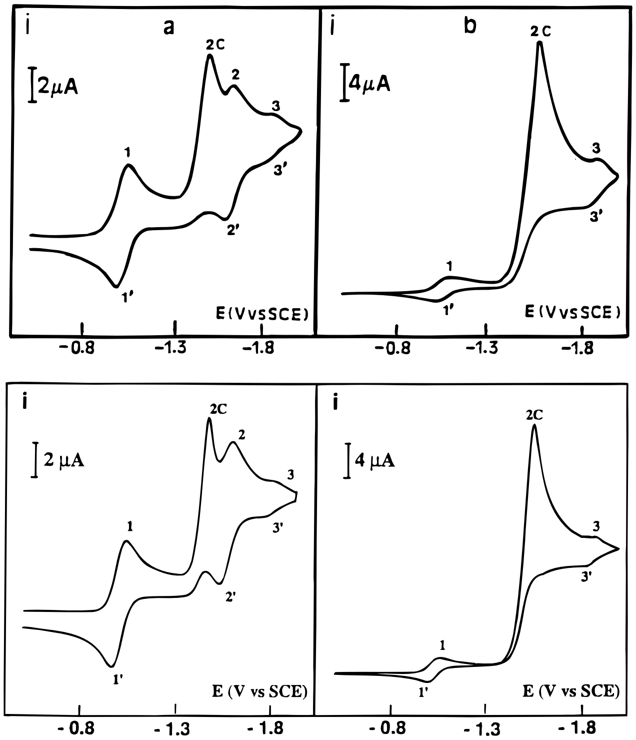

Figure 1. Cyclic voltammetry of TPPFe(III)Cl (a, 0.96 mM; b, 0.65 mM) in DMF + 0.1 M Et_4NClO_4 at a mercury drop hung to a 1 mm diameter gold disk in the presence of $Et_3NH^+Cl^-$ (a, 1.6 mM; b, 7.1 mM). Scan rate: 0.1 V/s. Temperature: 25 °C. Top: experimental curves. Bottom: simulated curves.

Figure 2 summarizes the results of a preparative-scale catalytic reduction of the acid. The observed faradaic yields show that the formation of hydrogen is totally selective. Another noteworthy result is that there is no significant degradation of the porphyrin catalyst after 1 h of electrolysis and passage of 70 C.

What about the mechanism of the catalytic reaction? One may think of two different types of catalysis. In one of them, addition of a proton to the $PFe(0)^{2-}$ catalyst would involve the porphyrin ring, leading to the formation of the phlorin anion which would then react with a second acid molecule to produce H_2. The second alternative would involve the iron coordination sphere, namely the formation of the iron(II) hydride which would then react with a second acid molecule hence evolving H_2. The first of these alternatives appears unlikely in view of the observation we made that the complex resulting from the addition of two electrons to TPPCu(II) does not catalyze hydrogen evolution under the same conditions in spite of the fact that the standard potential of the $TPPCu(II)^-/TPPCu(II)^{2-}$

---

[1] Present address: Laboratoire de Bioénergétique and Ingéniérie des Proteines, UPR CNRS 9036, 31 Chemin J. Aiguier, 13009 Marseille, France.

[2] Concerning electrocatalysis of hydrogen evolution at metal electrodes, see: ref 2b and references therein. (b) Divisek, J.; Schimtz, H.; Steffen, B. *Electrochim. Acta* **1994**, *39*, 1723.

[3] Mairanovskii, S. G. *Catalytic and Kinetic Waves in Polarography*; Plenum, New York, 1968; pp 245−261.

[4] (a) Keita, B.; Nadjo,L.; Savéant., J-M. *J. Electroanal. Chem.* **1988**, *243*, 105. (b) Keita, B.; Nadjo, L. *Mater. Chem. Phys.* **1989**, *22*, 77.

[5] (a) Chao, T-H.; Espenson, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 129. (b) Connolly, P.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 2684.

[6] (a) Kellett, R. M.; Spiro, T. G. *Inorg Chem.* **1985**, *24*, 2373. (b) Kellett, R. M.; Spiro, T. G. *Inorg. Chem.* **1985**, *24*, 2378.

[7] (a) Collman, J. P.; Wagenknetcht, P. S.; Lewis, N. S. *J. Am. Chem. Soc.* **1992** *114*, 5665. (b) Collman, J. P.; Ha, Y.; Wagenknetcht, P. S.; Lopez, M-A.; Guilard, R. *J. Am. Chem. Soc.* **1993**, *115*, 9080. (c) Collman, J. P.; Wagenknetcht, P. S.; Hutchison, J. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1537.

[8] (a) Lexa, D.; Rentien, P.; Savéant, J-M.;. Xu, F. *J. Electroanal. Chem.* **1985**, *191*, 253. (b) Gueutin, C.; Lexa, D.; Momenteau, M.; Savéant, J-M.; Xu, F. *Inorg. Chem.* **1986**, *25*, 4294.

[9] (a) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J-M.; M'Halla, F.; Savéant, J-M. *J. Electroanal. Chem.* **1980**, *113*, 19. (b) Savéant, J-M.; Su, K. B. *J. Electroanal. Chem.* **1984**, *171*, 341.

0002-7863/96/1518-3982$12.00/0 © 1996 American Chemical Society

couple (−1.63 V vs SCE) is almost the same as the standard potential of the $TPPFe(I)^-/TPPFe(0)^{2-}$ couple (−1.60 V vs SCE). Instead, addition of the acid leads to a $3e^- + 3H^+$ hydrogenation of the ring. The intermediacy of the iron(II) hydride is attested by the appearance of the small reversible wave 3/3′ with a standard potential of −1.88 V vs SCE for the $TPPFe(II)H^-/TPPFe(I)H^{2-}$ couple, which is close to the value −1.950 V vs SCE found for the $TPPFe(II)Et^-/TPPFe(I)Et^{2-}$ couple and −1.956 V vs SCE found for the $TPPFe(II)n\text{-}Bu^-/TPPFe(I)n\text{-}Bu^{\ 2-}$ couple in the same medium.[10]

Starting from TPPFe(II), the following reaction mechanism can thus be proposed.

$$PFe(II) + e^- \rightleftharpoons PFe(I)^- \qquad (E^0 = -1.03_5 \text{ V vs SCE})$$

$$PFe(I)^- + e^- \rightleftharpoons PFe(0)^{2-} \qquad (E^0 = -1.60_0 \text{ V vs SCE})$$

$$PFe(0)^{2-} + AH^+ \xrightarrow{2 \times 10^8\ M^{-1}\ s^{-1}} PFe(II)H^- + A$$

$$PFe(II)H^- + AH^+ \xrightarrow{4 \times 10^5\ M^{-1}\ s^{-1}} H_2 + PFe(II) + A$$

$$PFe(II)H^- + e^- \rightleftharpoons PFe(I)H^{2-} \quad (E^0 = -1.95_0 \text{ V vs SCE})$$

$$PFe(I)H^{2-} + AH^+ \rightarrow H_2 + PFe(I)^- + A$$

$$PFe(II) + PFe(0)^{2-} \rightarrow 2PFe(I)^- \qquad (\Delta G^0 = -0.56_5 \text{ eV})$$

$$PFe(II) + PFe(I)H^{2-} \rightarrow PFe(I)^- + PFe(II)H^- \qquad (\Delta G^0 = -0.91_5 \text{ eV})$$

$$PFe(I)^- + PFe(I)H^{2-} \rightarrow PFe(0)^{2-} + PFe(II)H^- \qquad (\Delta G^0 = -0.28_0 \text{ eV})$$

As seen in Figure 1, simulation of the cyclic voltammograms according to the above mechanism with the indicated values of the rate constants of the two key protonation steps and of the various standard potential satisfactorily reproduces the experimental kinetics. The reaction of the acid with the reduced form of the iron hydride, $PPFe(I)H^{\ 2-}$, to produce hydrogen is expected to be faster than the reaction with $PFe(II)H^-$. In the simulation, its rate constant was taken as equal to the diffusion limit. The exact value of this rate constant is in fact unimportant since, as seen in the simulations in figure 1, this reaction, even very fast, does not hamper the reversibility of the 3/3′ wave. This is because catalysis is so strong at the 2/2′ wave that, beyond this wave, the concentration of acid in the catalytic reaction layer is vanishingly small as expected under total catalysis conditions.[8] The last three homogeneous electron transfer reactions have all strong driving forces and involve small reorganization energies. Their rate constants have thus been taken as equal to the diffusion limit in the simulation.

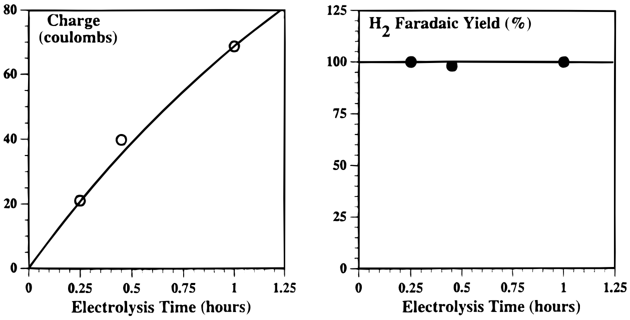

Figure 2. Catalysis of H_2 evolution by TPPFe(III)Cl (1 mM) in the preparative scale electrolysis of $Et_3NH^+Cl^-$ (50 mM) in DMF + 0.1 M Et_4NClO_4 at a mercury pool electrode. Electrolysis potential: −1.60 V vs SCE. Electrode surface area: 9.6 cm^2. Solution volume: 17 cm^3. Temperature: 25 °C. The quantity of H_2 formed was determined by gas chromatography (2 m length; 2.2 mm diameter stainless steel column filled with 60/80 Carbosieve S; oven temperature, 85 °C, carrier gas, He) after checking the propotionality between the peak surface area and the injected H_2 quantity.

In the catalysis reaction scheme above, the rate-limiting step of H_2 evolution is the reaction of $PFe(II)H^-$ with a second acid molecule. Since this is a fast reaction, $k = 4\ 10^5\ M^{-1}\ s^{-1}$, H_2 evolution is in fact limited by the diffusion of the acid to the electrode surface. The time constant of the cell used to obtained the results displayed in figure 2 is 0.54 h^{-1} (continuous line in the left-hand diagram), thus limiting the turnover number to 22 after 1 h of electrolysis. Optimization of the cell surface area-to-volume ratio could improve these figures by a factor of 100.

In conclusion, iron(0) porphyrins are remarkably efficient and persistent catalysts of electrochemical hydrogen evolution. These results provide a striking confirmation that iron(0)[11] porphyrins are able to develop a strong reactivity toward acids and electrophiles in the coordination sphere of iron at the expense of ring reduction as has previously been shown to be the case with alkyl halides[10b,12] and carbon dioxide.[13] With reference to hydrogenases, it is clear that the standard potential of the catalyst couple (−1.46 V vs aqueous NHE) is far beyond biological potentials. It is however worth noting that the catalytically active iron(0) porphyrin complex bears some resemblance with complexes where substantial electron density at the iron atom is transferred from sulfur ligands.

JA954326X

---

(10) (a) Gueutin, C. Thèse Université Paris 7 1991. (b) Gueutin, C.; Lexa, D.; Savéant, J-M.; Wang, D. L. *Organometallics* **1989**, *8*, 1607. (c) The fact that iron(II) hydrides are easier to reduce than iron (II) σ-alkyl complexes derives from the electron-donating properties of the alkyl ligand as compared to hydrogen. This is the same reason that aldehydes are easier to reduce than ketones.

(11) Anxolabéhère, E.; Chottard, G.; Lexa, D. *New J. Chem.* **1994**, *18*, 889.

(12) Lexa, D.; Savéant, J-M.; Wang, D. L. *Organometallics* **1986**, *5*, 1428. (b) Lexa, D.; Savéant, J-M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1988**, *110*, 7617.

(13) (a) Hammouche, M.; Lexa, D.; Savéant, J-M.; Momenteau, M. *J. Electroanal. Chem.* **1988**, *249*, 347. (b) Hammouche, M.; Lexa, D.; Momenteau, M.; Savéant, J-M. *J. Am. Chem. Soc.* **1991**, *113*, 8455. (c) Bhugun, I.; Lexa, D.; Savéant, J-M. *J. Am. Chem. Soc.* **1994**, *116*, 5015. (d) Bhugun, I.; Lexa, D.; Savéant, J-M., submitted for publication.