J. Am. Chem. Soc. 1994, 116, 5015–5016

Ultraefficient Selective Homogeneous Catalysis of the Electrochemical Reduction of Carbon Dioxide by an Iron(0) Porphyrin Associated with a Weak Brönsted Acid Cocatalyst

Iqbal Bhugun, Doris Lexa, 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 March 7, 1994

Heterogeneous and homogeneous catalysis of the electrochemical reduction of carbon dioxide has continued to receive active attention during the past few years.[1,2] There are two types of homogeneous catalysis of electrochemical reactions. In redox catalysis,[3] the reduced form of the catalyst couple is merely an outer-sphere electron donor that shuttles electrons from the electrode to the substrate. This homogeneous electron transfer is subject to the same Marcus-type limitations as the outer-sphere electron transfer at an inert electrode. The very existence of a catalytic effect thus derives from a physical rather than a chemical process, namely, the dispersion of the electrons in the same three-dimensional space as the substrate instead of the two-dimensional availability of the electrons at the electrode surface.[3] In chemical catalysis,[3] the interactions between the reduced form of the catalyst and the substrate are more intimate, involving the transient formation of an addition product between the reduced form of the catalyst and the substrate before regeneration of the oxidized form of the catalyst.

Direct electrochemical reduction of CO_2 at inert electrodes, such as mercury or lead, in low-acidity solvents, such as *N,N'*-dimethylformamide (DMF), yields a mixture of oxalate, formate, and carbon monoxide[4a] whereas formic acid is the main product in water.[4b] Redox catalysis in DMF by the anion radicals of benzonitrile,[5a] benzoic esters, their substituted analogues, and phthalic esters[5b] yields exclusively oxalate.[5c]

Low-valent states of transition-metal complexes have been extensively investigated as possible homogeneous chemical catalysts of CO_2 reduction. Faster catalyses than with redox catalysts of the same standard potentials are anticipated since Marcus-type limitations should not apply. Selectivity should also be improved as a consequence of CO_2 transformation taking place in the coordination sphere of the metal. CO is indeed often the main reduction product in electrochemical reductions of CO_2 catalyzed by transition-metal complexes such as Re, Rh, and Ru with 2,2'-bipyridine or similar ligands,[6] Co and Ni with nonporphyrinic macrocyclic ligands such as cyclams,[7] and Co and Fe porphyrins.[2,8] It should be noted, however, that in several of these cases, as with nickel cyclams[7c,d] and ruthenium bipyridine complexes,[6c] catalysis is not homogeneous but rather involves an adsorbed state of the complex.

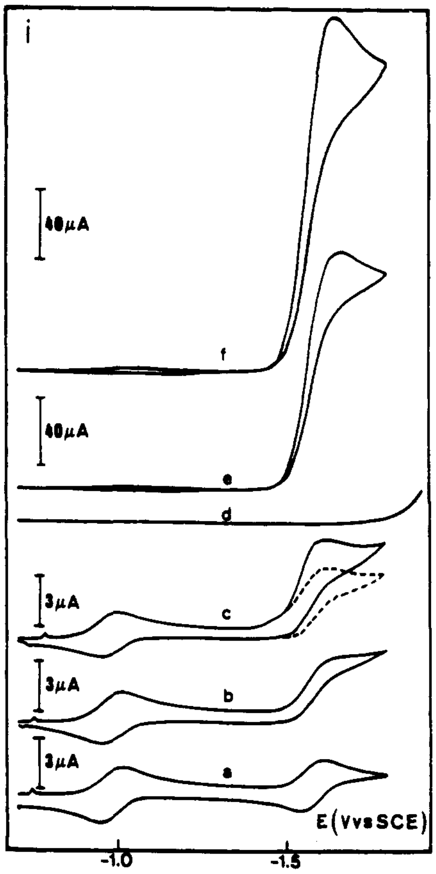


Figure 1. Cyclic voltammetry of iron tetraphenylporphyrin (1 mM) in DMF and 0.1 M Et_4ClO_4 at a hanging mercury drop electrode: (a) in the absence of CO_2 and CF_3CH_2OH; (b) in the presence of 1 atm of CO_2 (0.235 M[11]) and the absence of CF_3CH_2OH; (c) in the absence of CO_2 and the presence of 5.7% (0.78 M) CF_3CH_2OH (dashed line) and of 10.7% (1.47 M) CF_3CH_2OH (full line); (d) same solution as in e and f but in the absence of porphyrin; (e) in the presence of 1 atm of CO_2 and 0.78 M CF_3CH_2OH; (f) in the presence of 1 atm of CO_2 and 1.47 M CF_3CH_2OH. Scan rate: 0.1 V/s. Temperature: 20 °C. Similar results were found at a glassy carbon disk electrode.

Iron tetraphenylporphyrin catalyzes the electrochemical reduction of CO_2 at the Fe^I/Fe^0 wave in DMF. However, the catalytic efficiency[9] is very low and the porphyrin catalyst is rapidly consumed during preparative-scale electrolysis.[2] Addition of Mg^{2+} ions to the solution dramatically improved the catalytic efficiency,[9] which may rise to values as high as 20, and to a CO turnover number reaching 10 per hour. The stability of the catalyst was also greatly enhanced. The faradaic yield in CO was around 60–70%,[2a] the remainder being formate.[10] Other Lewis acids, such as Li^+, Na^+, Ba^{2+}, and Al^{3+} ions, were also shown to improve the catalysis, albeit to a lesser extent.[2a,10a]

---

(1) (a) For reviews, see refs 1b and 1c and also the introduction of ref 2a. (b) Silvestri, G. In *Carbon Dioxide as a Source of Carbon*; Aresta, M., Forti, G., Eds.; NATO ASI Series, Ser. C; Reidel: Dordrecht, 1987; pp 339. (c) Collin, J. P.; Sauvage, J. P. *Coord. Chem. Rev.* **1989**, *93*, 245.

(2) (a) Hammouche, M.; Lexa, D.; Momenteau, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1991**, *113*, 8455. (b) Hammouche, M.; Lexa, D.; Savéant, J.-M.; Momenteau, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *249*, 347.

(3) (a) Andrieux, C. P.; Dumas-Bouchiat, J.-M.; Savéant, J.-M. *J. Electroanal. Chem.* **1978**, *87*, 39. (b) Andrieux, C. P.; Savéant, J.-M. Electrochemical Reactions. In *Investigations of Rates and Mechanisms*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. 6, 4/E, Part 2, p 305. (c) Andrieux, C. P.; Hapiot, P.; Savéant, J.-M. *Chem. Rev.* **1990**, *90*, 723.

(4) (a) See refs 3a–g in ref 2a. (b) See refs 4 in ref 2a.

(5) (a) Filardo, G.; Gambino, S.; Silvestri, G.; Gennaro, A.; Vianello, E. *J. Electroanal: Chem. Interfacial Electrochem.* **1984**, *177*, 303. (b) Vianello, E. Private Communication. (c) The other aromatic anion radicals classically used in redox catalysis in aprotic solvents couple with the $CO_2^{•-}$ anion radical leading to a hydrocarboxylation reaction that destroys the catalyst. Rather than catalysis of the CO_2 reduction, the interest of such reactions is to offer a procedure for introducing CO_2 gropus into organic molecules.[1b]

(6) (a) See refs 13 in ref 2a. (b) Lehn, J. M.; Ziessel, R. *J. Organomet. Chem.* **1990**, *382*, 157. (c) Ishida, H.; Fujuki, K.; Ohba, T.; Ohkubo, K.; Tanaka, K.; Terada, T.; Tanaka, T. *J. Chem. Soc., Dalton Trans.* **1990**, 2155.

(7) (a) See refs 12 in ref 2a. (b) Fujihira, M.; Nakmura, Y.; Hirata, Y.; Akiba, U.; Suga, K. *Denki Kagaku* **1991**, *59*, 532. (c) Balazs, G. B.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1992**, *332*, 325. (d) Balazs, G. B.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1993**, *361*, 149.

(8) See refs 11c–g in ref 2a.

(9) Defined by the ratio, i_p/i_p^0, of the cyclic voltammetric peak or plateau currents in the presence and absence of the substrate, respectively.

(10) (a) Bhugun, I.; Lexa, D.; Savéant, J.-M., unpublished data. (b) CO and H_2 were titrated by gas chromatography as described in ref 2a. Formate was determined by ionic chromatography.

(11) Gennaro, A.; Isse, A. A.; Vianello, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *289*, 203.

0002-7863/94/1516-5015$04.50/0

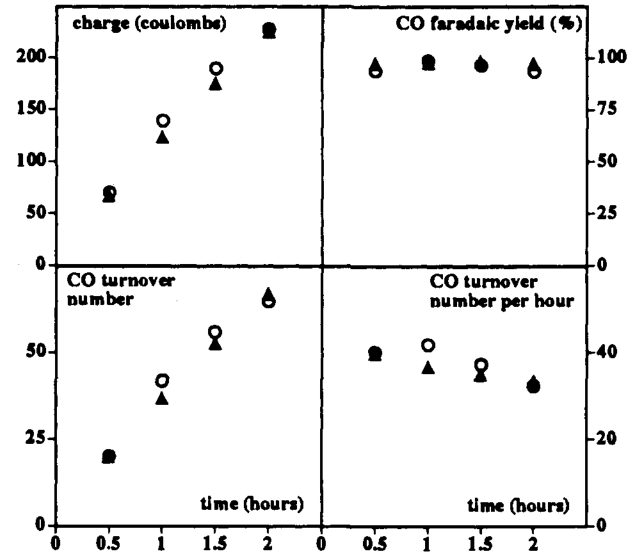


Figure 2. Preparative-scale electrolysis of CO_2 (1 atm) catalyzed by iron tetraphenylporphyrin (1 mM) in DMF and 0.1 M Et_4ClO_4 at a mercury pool electrode in the presence of 0.55 M (○) and of 1.35 M (▲) CF_3CH_2OH. Electrolysis potential: −1.70 V vs SCE. Temperature: 25 °C.

Are Brönsted acids similarly able to increase both the catalytic efficiency and the selectivity? We have now found that the addition of alcohols does result in such an improvement. A typical example is provided by trifluoroethanol (CF_3CH_2OH). As seen in Figure 1a,b, the catalytic increase of the wave is very modest in a pure DMF solution ($i_p/i_p^0 = 1.8$). The addition of 0.78 M CF_3CH_2OH results in a large increase of the Fe^I/Fe^0 wave (Figure 1e), i_p/i_p^0 reaching a value of 81. With the addition of 1.47 M CF_3CH_2OH, the catalytic efficiency reaches the unprecedented value of 131 (Figure 1f).

Starting from a reversible Fe^I/Fe^0 wave (Figure 1a), one notices that the addition of CF_3CH_2OH to the solution renders the wave irreversible and increases its height (Figure 1c), indicating either a reductive saturation of the porphyrin ring or a catalysis of hydrogen evolution by the Fe^0 porphyrin. These reactions do not prevent the catalysis of CO_2 reduction from occurring (Figure 1e,f). This is confirmed by the results of preparative-scale electrolyses where excellent faradaic yields in CO were found with no trace of hydrogen evolution.[10b] In two typical experiments, where 4% (0.55 M) and 10% (1.35 M) CF_3CH_2OH, respectively, were added to the solution, the variation with time of the charge passed through the electrode, the CO faradaic yield, the CO turnover number, and the CO turnover number per hour were as summarized in Figure 2. The electrolysis cell was as described in reference 2a using a mercury pool as working electrode, but the unseparated magnesium anode was replaced by a separated anodic compartment containing a platinum grid electrode and a 0.49 M solution of tetraethylammonium acetate and 0.13 M Et_4ClO_4 (the anodic reaction is then the formation of CO_2 and C_2H_6 according to the classical Kolbe reaction.)

In both cases, CO was the only product with a faradaic yield over 94%. High values of the turnover number per hour thus reached become independent of the CF_3CH_2OH concentration because the current is so high that it is limited by the cell geometry. The turnover number per hour is observed to slowly decay as a result of the degradation of the porphyrin as checked by cyclic voltammetry of the electrolyzed solutions. For the same amount of CO_2 converted into CO, the degradation diminishes upon increasing the amount of CF_3CH_2OH: the porphyrin loss is 40% with 4% CF_3CH_2OH and only 25% with 10% CF_3CH_2OH after the passage of the same charge, namely, 225 C.

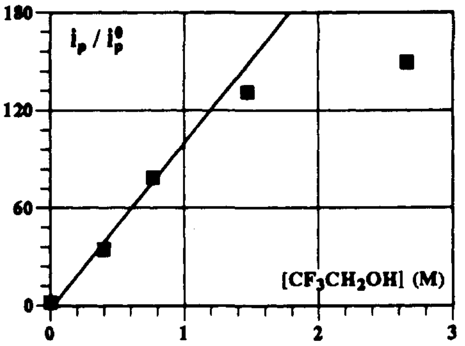
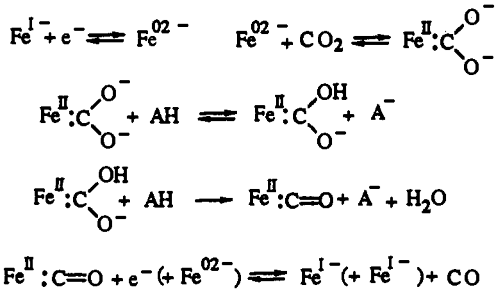


Figure 3. Cyclic voltammetry of iron tetraphenylporphyrin (1 mM) in DMF and 0.1 M Et_4ClO_4 at a hanging mercury drop electrode in the presence of 1 atm of CO_2. Variation of the catalytic efficiency, i_p/i_p^0,[9] with the amount of CF_3CH_2OH added. Scan rate: v = V/s. Temperature: 20 °C.

Scheme 1



Turning back to cyclic voltammetry, the variations of i_p/i_p^0 with the concentration of CF_3CH_2OH exhibit first a linear behavior (Figure 3). Since, within this range of concentrations,[2a,3b] $i_p/i_p^0 \approx (k_{app}[CO_2])^{1/2}/0.446\ (Fv/RT)^{1/2}$ it follows that the apparent rate constant, k_{app}, varies as $[CF_3CH_2OH]^2$, suggesting the reaction mechanism depicted in Scheme 1 (where A = CF_3CH_2O).

The $CF_3CH_2O^-$ ions thus formed may react with CO_2, leading to a mixture of CO_3^{2-}, $HOCO_2^-$, and $CF_3CH_2OCO_2^-$. However, GC titration of the alcohol at the end of the electrolysis revealed that its consumption is negligible.

Work is currently in progress to ascertain the mechanism by which this type of weak Brönsted acid interferes in the catalysis, to optimize the conditions for preparative-scale electrolyses, and to vary the nature and pK_a of the acid. In this connection preliminary results indicate that acceleration of catalysis is also observed with 1-propanol and that with significantly stronger acids, such as Et_3NH^+, hydrogen evolution is strongly catalyzed by the Fe^0 porphyrin.