One- and Two-electron Pathways in the Electrocatalytic Reduction of CO_2 by fac-Re(bpy)(CO)$_3$Cl (bpy = 2,2'-bipyridine)

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The cyclic voltammetry of fac-Re(bpy)(CO)$_3$Cl (bpy = 2,2'-bipyridine) and of the intermediate complexes formed by bulk electrolysis in MeCN solution in the presence and absence of CO_2 has been interpreted in terms of two different electrocatalytic pathways for the reduction of CO_2 to CO, one involving an initial one-electron reduction and the other an initial two-electron reduction.

Few electrocatalytic systems for the reduction of CO_2 are known based on transition metal complexes.[1—9] A particularly efficient example,[10] fac-Re(bpy)(CO)$_3$Cl, (bpy = 2,2'-bipyridine) has been reported by Hawecker, Lehn, and Ziessel. We report here the results of an electrochemical study of fac-Re(bpy)(CO)$_3$Cl and related derivatives, which defines two independent pathways for the electrocatalytic reduction of CO_2 to CO. Remarkably, in the one-electron pathway, a *net* two-electron reduction of CO_2 to CO is initiated by a one-electron step.

Figure 1 shows reductive cyclic voltammograms (c.v.'s) of fac-Re(bpy)(CO)$_3$Cl in MeCN solution with 0.1 M tetrabutyl-ammonium hexafluorophosphate (TBAH) as supporting electrolyte. From previous work on this and related complexes,[11,12] the redox potential for the first reduction (marked process A, Figure 1) is relatively insensitive to replacing chloride with other ligands L. The insensitivity to L, and the similarity in potential to the first reduction process in [Ru(bpy)$_3$]$^{2+}$ {cf., fac-Re(bpy)(CO)$_3$Cl, $E_{\frac{1}{2}}$ = −1.35 V; [Ru(bpy)$_3$]$^{2+}$, $E_{\frac{1}{2}}$ = −1.29 V, in MeCN solution vs. saturated calomel electrode, s.c.e.} both point toward process A being an initial localized bpy reduction.
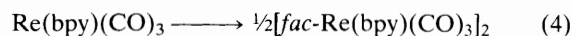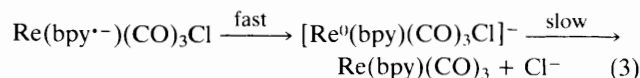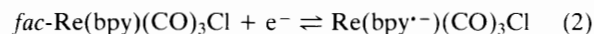
The second, irreversible reduction process (C, Figure 1) is assigned to a metal-based reduction because of the sensitivity of the peak potential to ligand variation. For example, in the series fac-Re(bpy)(CO)$_3$L^{n+} where L = 4-ethylpyridine ($n = 1$), Cl$^-$ ($n = 0$), and hydride ($n = 0$) the peak potentials at a sweep rate of 100 mV s^{-1} are −1.54, −1.71, and > −2.1 V vs. s.c.e., respectively.

Coulometry and bulk electrolytic reduction at −1.40 V to −1.50 V (vs. s.c.e.) in MeCN with 0.1 M TBAH as supporting electrolyte demonstrated that wave A is a one-electron reduction but that it is coupled to the formation of the sparingly soluble, green dimer [fac-Re(bpy)(CO)$_3$]$_2$. This

dimer was characterized by u.v.-visible, i.r., and ^{1}H n.m.r. spectroscopy and elemental analysis. Its formulation was further supported by independent synthesis in *ca.* 40% yield from Re$_2$(CO)$_{10}$ (equation 1) and by comparison of its properties with the known 1,10-phenanthroline (phen) analogue, [fac-Re(phen)(CO)$_3$]$_2$.[13]

$$Re_2(CO)_{10} + 2bpy \xrightarrow[\text{3 days}]{\text{xylenes, reflux}}$$

$$[fac\text{-}Re(bpy)(CO)_3]_2 + 4CO \quad (1)$$
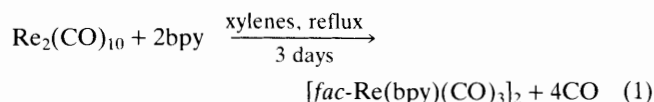
The c.v.'s in Figure 1, lower curves, were obtained at a scan rate of 200 mV s^{-1}, and are reversible at the initial one-electron wave (waves A,F), indicating that dimer formation is slow on the voltammetric timescale. Given the slow rate of Cl$^-$ loss, ligand loss may be preceded by intramolecular electron transfer to a metal-based dσ^* orbital, which would provide a basis for metal–metal bond formation (equations 2—4). Thus the overall reduction at the first wave is that shown in equation (2).

$$fac\text{-}Re(bpy)(CO)_3Cl + e^- \rightleftharpoons Re(bpy^{\cdot-})(CO)_3Cl \quad (2)$$

$$Re(bpy^{\cdot-})(CO)_3Cl \xrightarrow{\text{fast}} [Re^0(bpy)(CO)_3Cl]^- \xrightarrow{\text{slow}}$$
$$Re(bpy)(CO)_3 + Cl^- \quad (3)$$

$$Re(bpy)(CO)_3 \longrightarrow \tfrac{1}{2}[fac\text{-}Re(bpy)(CO)_3]_2 \quad (4)$$

Coulometry at −1.8 V, past the second, metal-based wave (C, Figure 1) consumed two electrons per Re to give an intense red–purple solution which we believe to be [Re(bpy)(CO)$_3$]$^-$ by analogy to the known 1,10-phen analogue and its associated redox behaviour.[13] The anion could also be generated directly, and quantitatively, from [fac-

Figure 1. C.v.'s of *fac*-Re(bpy)(CO)₃Cl in MeCN solution with TBAH as supporting electrolyte using a Pt button electrode taken at a sweep rate of 200 mV s⁻¹. The lower c.v.'s show the switching potential characteristics of the coupled chemical reactions. The lettered redox processes are discussed in the text. The upper curves show the effect of CO₂ (at saturation) on the c.v.

Scheme 1.

A = an oxide ion acceptor

Re(bpy)(CO)₃]₂ by bulk electrolysis at −1.60 V [*n* = 1.94; dimethylformamide (DMF) solution]. Immediate reoxidation of this solution at −0.6 V led to the dimer again with *n* = 1.51.

The dimer-anion pseudo-couple undoubtedly accounts for some of the complexities in the c.v. in the lower curves in Figure 1. In particular, as shown by the dashed line, initiation of a second cyclical scan at −1.35 V, leads to a new reductive wave, feature B, which is, in turn, coupled to oxidative wave D which appears following scan reversal at potentials more negative than *ca.* −1.6 V. The origin of the B,D redox couple is, in fact, the dimer-anion pseudo-couple shown in equation (5).

$$[fac\text{-Re(bpy)(CO)}_3]_2 \underset{-2e^-}{\overset{+2e^-}{\longleftrightarrow}} 2[\text{Re(bpy)(CO)}_3]^- \quad (5)$$

The dashed line in the upper part of Figure 1 shows the first scan c.v. of *fac*-Re(bpy)(CO)₃Cl in CO₂-saturated MeCN. Reductive scans show that little or no catalytic enhancement occurs at the bpy-based reduction potential at a scan rate of 200 mV s⁻¹ and that the onset of the catalytic current occurs at

−1.4 V and continues through the potential region characteristic of the second reduction of *fac*-Re(bpy)(CO)₃Cl and of the two-electron reduction of [*fac*-Re(bpy)(CO)₃]₂.

Constant potential electrolyses of solutions containing 3—4 mM of *fac*-Re(bpy)(CO)₃Cl in freshly distilled, CO₂-saturated MeCN at −1.5 to −1.55 V *vs.* s.c.e. resulted in sustained electrocatalysis. Typically, product analysis was undertaken after 50—100 C of current had passed and only CO and CO₃²⁻ were detected as products (equation 6). The current efficiency for the production of CO averaged 98% and for CO₃²⁻ 112%; the latter value arises from a large experimental uncertainty associated with carbonate analysis.

$$2CO_2 + 2e^- \xrightarrow[-1.50\,V]{\text{MeCN}} CO + CO_3^{2-} \quad (6)$$

Electrolyses of solutions containing 2—4 mM *fac*-Re(bpy)(CO)₃Cl past the metal-based reduction wave in CO₂-saturated MeCN or DMF or of [*fac*-Re(bpy)(CO)₃]₂ in CO₂-saturated DMF at −1.8 V (0.1 M TBAH) also resulted in the production of CO with current efficiencies >85%. Product analysis of the solution showed no CO₃²⁻ but small amounts of NBuⁿ₃. Previous work has shown that amine formation from highly basic conditions generated during electrocatalytic CO₂ reduction is a result of quaternary ammonium salt fragmentation reactions *via* Hofmann degradation.[4,9]

Such electrochemical results point convincingly to the existence of at least two distinct pathways for the reduction of CO₂ by *fac*-Re(bpy)(CO)₃Cl, as shown in Scheme 1. The first involves the intermediacy of the radical Re(bpy)(CO)₃ or its solvated form Re(bpy)(CO)₃MeCN. Furthermore, production of the insoluble [*fac*-Re(bpy)(CO)₃]₂ dimer is completely suppressed in CO₂-saturated solution, showing that CO₂ intercepts the reduced species present and that subsequent, more rapid CO₂ reduction steps occur. This conclusion is supported by the fact that photolysis of the dimer [*fac*-Re(bpy)(CO)₃]₂, in CO₂-saturated dimethyl sulphoxide also gives CO and interestingly, *fac*-Re(bpy)(CO)₃(OCO₂H). We presume that the photochemical reaction involves initial Re–Re bond cleavage (equation 7), followed by entry of the

$$[\textit{fac}\text{-Re(bpy)(CO)}_3]_2 \xrightarrow{h\nu} 2\ \textit{fac}\text{-Re(bpy)(CO)}_3 \quad (7)$$

monomers into the CO_2 reduction cycle, a point that is currently under investigation by flash photolysis.

The products of the 'one-electron pathway,' CO and $CO_3{}^{2-}$ are those which occur with a variety of other reductants perhaps most notably with group 6 carbonyl anions.[14]

The second two-electron pathway for CO_2 reduction involves the anion $[\text{Re(bpy)(CO)}_3]^-$ and results in the production of CO from CO_2 with high current efficiency, although the ultimate fate of the oxide ion released is still unknown.

The results of our electrochemical studies are summarized in Scheme 1 where the one- and two-electron pathways are explicity shown. Although we have no direct evidence for the intermediate CO_2 complexes, their existence is inferred by our observations. With regard to their electronic structure it should be realized that redox processes can take place at the bpy ligand ($\text{bpy}^{0/-}$ couple), at the metal ($\text{Re}^{I/0}$ couple), or at the co-ordinated carbon dioxide ($CO_2{}^{0/-}$ couple).[15] Only by understanding the chemical properties associated with the charge distributions within the CO_2 complexes will a more complete understanding of the electrocatalytic behaviour be attained.

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