Electrocatalytic Reduction of Carbon Dioxide Mediated by Re(bipy)(CO)$_3$Cl (bipy = 2,2′-bipyridine)

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Re(bipy)(CO)$_3$Cl (bipy = 2,2′-bipyridine) is an efficient homogeneous catalyst for the selective and sustained electrochemical reduction of CO_2 to CO at low potential.

The reduction of carbon dioxide, a process of fundamental importance from the standpoints of both chemical activation and fuel generation, requires the discovery of catalysts providing low energy, polyelectronic reaction pathways of high efficiency (refs. 1—3 and references therein).

We have recently described two photochemical systems, which employ homogeneous transition metal catalysts, [Ru(bipy)$_3$Cl$_2$ + CoCl$_2$][3] or Re(bipy)(CO)$_3$X (bipy = 2,2′-bipyridine) (X = Cl, Br),[4] for generating (CO + H_2) or (CO + formate) respectively under visible light irradiation. The same catalytic species could also operate when the energy required is provided by applying an electric potential rather than by light absorption.

Direct non-catalysed electroreduction of CO_2 follows a monoelectronic pathway requiring potentials as negative as about −2 V.[5,6] Numerous studies have been conducted employing various electrode materials and solvent media (see *e.g.* refs. 6—8). On the other hand, polyelectronic reduction of CO_2 may occur at much less negative potentials; in particular dielectronic reduction to CO requires only −0.52 V at pH 7 [equation (1)].[3,5]

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O \qquad (1)$$

Thus, a major problem resides in finding catalysts capable of facilitating such polyelectronic reactions. The use of porphyrin and phthalocyanine complexes[9] as well as iron–sulphur clusters[10] has been investigated; nickel and cobalt complexes of macrocyclic polyamines were recently shown to act as electrocatalysts, generating CO from CO_2 (together with H_2 from H_2O) at potentials between *ca.* −1.1 and −1.4 V *vs.* N.H.E. (N.H.E. = Normal hydrogen electrode).[11]

We report here that Re(bipy)(CO)$_3$Cl, the catalyst used previously for CO_2 photoreduction,[4] is also a highly active homogeneous catalyst for the electrochemical reduction of CO_2 to CO.

When a dimethylformamide (DMF)–water (9 : 1) solution (60 ml) containing 2 mg Re(bipy)(CO)$_3$Cl, 0.1 M Et$_4$NCl and saturated with CO_2 was electrolysed on a glassy carbon electrode at −1.25 V *vs.* N.H.E. during 14 h, about 32 ml of CO were produced with 98% current efficiency. A number of experiments were performed in order to investigate the features of the reaction and some of the results obtained are listed in Table 1.

(i) The process represents an electrochemical reduction of CO_2 to CO at a potential of −1.25 V *vs.* N.H.E, *i.e.* substantially below the potential for direct CO_2 reduction. No CO (< 0.1 µl) is obtained when the electrolysis is performed in the absence of either metal complex or CO_2.

(ii) The reaction is catalytic in rhenium complex with large turnover numbers; it displays high current efficiency and high stability, the production of CO depending linearly on time or number of coulombs consumed (Figure 1). In a long term experiment (expt. 1, Table 1), the rhenium complex underwent 300 catalytic cycles without loss of activity in 14 h and

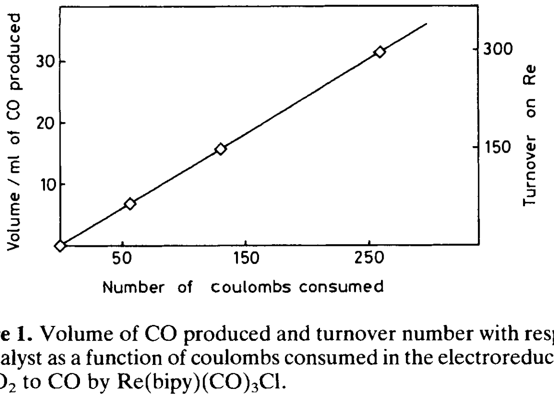

Figure 1. Volume of CO produced and turnover number with respect to catalyst as a function of coulombs consumed in the electroreduction of CO_2 to CO by Re(bipy)(CO)$_3$Cl.

Table 1. Electroreduction of CO_2 catalysed by $Re(bipy)(CO)_3Cl$ in $DMF–H_2O$ solutions.[a]

Expt.	Medium composition	Electrolysis time/h	Volume of CO produced/ml	Coulombs consumed	Average current efficiency %[b]
1[c]	$DMF–H_2O$ (10%)–NBu_4ClO_4	3	6.8	55.6	
	"	7	15.8	129.5	98
	"	14	31.6	259.9	
2	DMF–NEt_4Cl	1	0.96	8.3	
	"	2	1.7	14.9	
	"	3	2.4	20.9	92
	"	4	2.9	25.9	
	"	5	3.1	28.1	
3	$DMF–H_2O$ (5%)–NEt_4Cl	1	1.6	13.8	
	"	2	3.0	25.9	
	"	3	4.6	40.2	93
	"	4	6.0	51.0	
4	$DMF–H_2O$ (10%)–NEt_4Cl	1	2.4	20.5	
	"	2	4.7	40.6	
	"	3.5	8.2	70.9	94
	"	5	11.7	100.1	
5	$DMF–H_2O$ (10%)–NBu_4ClO_4	1.5	3.6	31.5	
	"	3	7.2	61.6	94
	"	5	12.0	102.7	
6[d]	$DMF–H_2O$ (20%)–NEt_4Cl	1	1.6	14.3	
	"	2	3.2	28.3	91
	"	3.5	5.5	48.6	

[a] CO_2 (99.8% purity) saturated solution (60 ml) containing 25 mg of $Re(bipy)(CO)_3Cl$ (9.0×10^{-4} M) and 0.1 M supporting electrolyte was placed in a gas-tight electrolysis cell (three-necked, round-bottomed flask equipped with an oil valve); the working electrode in all the experiments was glassy carbon (*ca.* 10 cm^2). The connection to the working electrode was made with a Pt wire inserted through the lateral part of the flask. The total volume occupied by the gases in the electroysis cell was 130 ml. All the solutions were electrolysed at −1.25 V *vs.* N.H.E. and at *ca.* 25 °C. The gases were analysed by gas chromatography. [b] Averaged over the total duration of the experiment. Since the reduction product requires two electrons for its formation, 2 equivalents of electrons passed through the electrolysis cell afford 1 mole of CO. [c] Only 7.5×10^{-5} M $Re(bipy)(CO)_3Cl$ was used in this run. [d] In this experiment traces of H_2 were detected (about 10 µl after 3.5 hours). After this time a slight, as yet uncharacterized, precipitate appeared.

remained unchanged, as shown by isolation and characterization (t.l.c., ^{13}C n.m.r.) at the end of the run.

(iii) The process shows high selectivity, giving CO with very high current efficiency (Table 1); furthermore, no other product was observed by ^{13}C n.m.r. The reaction was unaffected when the Cl^- anion of the supporting electrolyte was replaced by ClO_4^-, and no rhenium–formate complex could be detected (t.l.c., ^{13}C n.m.r.), whereas it was formed in some photoreduction experiments using the same starting complex.[4,†]

Electroreduction of CO_2 with macrocyclic nickel and cobalt catalysts gives both CO and H_2,[11] like the photochemical reduction experiments using cobalt ions.[3]

(iv) Optimum efficiency is observed with 10% water in the medium (Table 1). Above this value traces of H_2 are generated, a yellow precipitate, as yet unidentified, is formed. When no water is added, coulomb consumption and CO production are much slower, levelling off after a few hours, and an orange species accumulates, which disappears slowly when the current is switched off. This orange species is also observed close to the cathode when operating under optimal conditions (*ca.* 10% water added); it then does not accumulate but reacts rapidly and may be considered as the active species in the CO_2 reduction. When the electrolysis is conducted in the absence of CO_2 (DMF–water 9 : 1 solution under argon), no CO is detected but H_2 is produced (4.5 ml in 5 h); again an orange substance is formed, which disappears on introduction of CO_2. This orange compound is probably a reduced complex, since cyclic voltammetry indicates that reversible monoelectronic reduction of $Re(bipy)(CO)_3Cl$ occurs at −1.12 V *vs.* N.H.E; its further characterization is in progress.

(v) On the basis of the present results a schematic and tentative reaction cycle may be suggested for the electrochemical reduction of CO_2 to CO catalysed by $Re(bipy)(CO)_3Cl$. Reduction of the latter to $[Re(bipy)(CO)_3Cl]^-$ is followed by reaction with CO_2, giving a Re^{II} complex which yields CO according to the overall equation (1) and regenerates the starting complex by reduction. The nature of these intermediate complexes and the details of the $CO_2 \rightarrow CO$ conversion are not known. Some preliminary observations as well as data obtained for the photochemical process[4] indicate that CO formation is promoted and formate production repressed by co-ordinating anions; this might mean that a formate results from reaction with a hydride formed at the anion co-ordination site, and that CO_2 fixation occurs at another site of the rhenium complex.

Further studies are in progress in order to clarify the mechanistic details of CO and formate generation from CO_2; they will also be relevant to the photochemical process reported earlier.[4]

The electrocatalytic CO_2 reduction system reported here represents a process for the chemical conversion and storage of electrical energy. Higher energy efficiency may be achievable by approaching more closely the thermodynamic redox potential of equation (1) *via* modification of the ligand in the rhenium complex or utilization of other metal complexes (of Mn, Fe, Co, Ru, W *etc.*). Finally, one may expect a significant

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[†] In comparison, when the $Ru(bipy)_2(DMF)_2^{2+}$, $2PF_6^-$ complex is used as a catalyst in place of $Re(bipy)(CO)_3Cl$ (under the conditions of expt. 5; see Table 1), electrolysis at −1.35 V (*vs.* N.H.E.; for 9 h) yields both CO (4.0 ml) and H_2 (8.7 ml) (22 mg complex; 101.5 coulombs consumed; 98% current efficiency).

gain in potential, with conversion of light energy, by performing photoelectroreduction of CO_2 in a system combining the present or other efficient catalysts with a photocathode.

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