Electrocatalytic Reduction of CO_2 based on Polypyridyl Complexes of Rhodium and Ruthenium

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Electrocatalytic reduction of CO_2 to either CO or formate ion in MeCN solution has been shown to occur using precursor complexes such as $Ru(trpy)(dppene)Cl^+$ or cis-$Rh(bpy)_2(TFMS)_2^+$ [trpy = 2,2′,2″-terpyridine; dppene = cis-1,2-bis(diphenylphosphino)ethylene; bpy = 2,2′-bipyridine; TFMS = trifluoromethanesulphonate anion].

Although an attractive approach to the reduction of CO_2, electrochemical techniques normally require large negative overvoltages (*e.g.*, in dimethylformamide, -2.21 V and in MeCN, -2.10 V *vs.* standard calomel electrode, S.C.E.).[1] There have been a few reports of the use of transition metal complexes as electrocatalysts for CO_2 reduction in homogeneous solution[2—7] and recent results based on semiconductor electrodes[8] and derivatized metal cathodes[9] have shown promise. We report here the electrocatalysed reduction of CO_2 based on transition metal complexes containing ligands such as 2,2′-bipyridine (bpy) or 2,2′,2″-terpyridine (trpy). Our results are significant in that: (i) they suggest that the problem of CO_2 reduction in homogeneous solution using soluble transition metal catalysts may be less formidable than once thought and accessible to a family of reducing agents; (ii) depending on the chosen system, CO or the formate ion may be selected as the reduction product; and (iii) they show the value of polypyridyl and perhaps other 'electron reservoir' ligands in providing the initial site of reduction.

Cyclic voltammetry (c.v.) experiments on a number of polypyridyl complexes in MeCN solution using tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte show reductive current enhancement between -1.2 and -1.7 V (*vs.* S.C.E.) in the presence of CO_2. Examples include $Rh(bpy)(COD)^+$ (COD = cyclo-octa-1,3-diene) $(-1.71$ V), cis-$M(bpy)_2(O_3SCF_3)^{2+}$ (M = Rh -1.5 V; M = Ir -1.59 V), $Ru(\eta^6$-$C_6H_6)(bpy)Cl^+$ $(-1.16$ V), $Ru(trpy)(dppene)Cl^+$ [dppene = cis-1,2-bis(diphenylphosphino)ethylene] $(-1.40$ V), and fac-$Re(bpy)(CO)_3$-$(MeCN)^+$ $(-1.45$ V).

We have examined two of these examples in detail, where the catalyst precursors are $Ru(trpy)(dppene)Cl^+$ and $Rh(bpy)_2(O_3SCF_3)^{2+}$. Controlled potential electrolysis (c.p.e.) experiments were performed in a cylindrical gas tight cell of our design under one atmosphere of CO_2. The concentration of the precursor complex ranged from 1.5 to 3.0 mM and the electrolyte–solvent system was 0.1 M TBAH in freshly distilled, dry MeCN. G.c. analysis was used to determine the composition of the gases above the solution after electrolysis and formate was determined by esterification to methyl formate followed by g.c. analysis of the solution phase. In all cases control experiments demonstrated that the observed products were, in fact, derived from CO_2.

Figure 1(a) shows the c.v. of cis-$Rh(bpy)_2(O_3SCF_3)^+$ which is similar to that reported for cis-$Rh(bpy)_2Cl_2^+$.[10] For both complexes an irreversible, metal localized, two electron reduction occurs at a potential which is sensitive to the nature of the halide or pseudohalide ligand; these are followed by two stepwise, one electron reductions to $Rh(bpy)_2^0$ $(-1.25$ V) and $Rh(bpy)_2^-$ $(-1.55$ V). In the presence of CO_2, current enhancement was observed only at the latter reduction wave. Electrolysis of a solution which was 2.5 mM in complex at -1.55 V with a carbon cloth electrode under an atmosphere of CO_2 resulted in a transient, intense purple solution associated with the presence of $Rh(bpy)_2^+$ followed by the formation of a green solution containing a small amount of solid
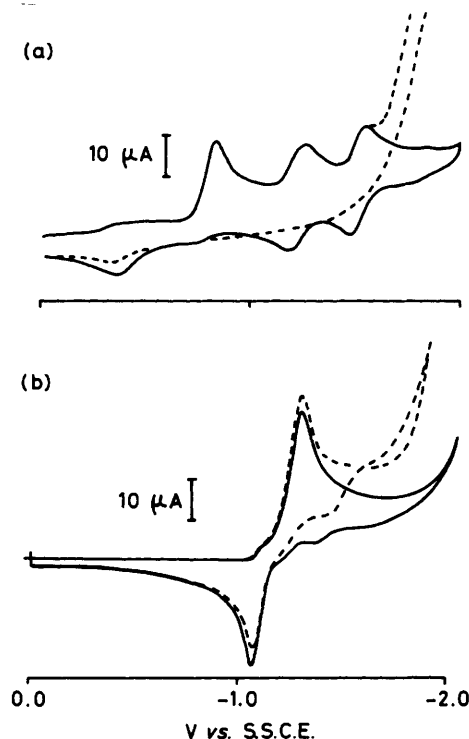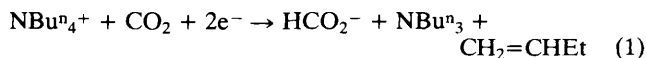

Figure 1. Cyclic voltammogram of (a) cis-$Rh(bpy)_2(O_3SCF_3)_2^+$ (b) $[Ru(trpy)(dppene)Cl]^+$ in MeCN with 0.1 M tetra-n-butylammonium hexafluorophosphate as supporting electrolyte using a Pt button working electrode at a scan rate of 200 mV s^{-1}. S.S.C.E. = saturated sodium chloride electrode. Solid lines are for complexes under an Ar atmosphere; dashed lines are for complexes under a CO_2 atmosphere (CO_2 saturated solution).

material. In one hour 77 C were passed and product analysis by g.c. showed the formation of H_2 (4.6×10^{-2} mM), formate (0.23 mM; analysed as methyl formate), tributylamine (*ca.* 0.30 mM), and a low boiling point component which is probably butene.

Correcting for the number of equivalents needed for the four-electron reduction of the initial Rh^{III} complex and noting that two electrons are required for the production of both formate and H_2, the current efficiencies were 64% and 12%, respectively. Since the sum of the yields of formate and H_2 is equal to that of tributylamine, the catalytic stoicheiometries in equations (1) and (2) can be written. A significant observation is that H_2 production in this system occurs only in the presence of CO_2.

$$NBu^n_4{}^+ + CO_2 + 2e^- \rightarrow HCO_2^- + NBu^n_3 + CH_2{=}CHEt \quad (1)$$

$$2NBu^n_4{}^+ + 2e^- \rightarrow H_2 + 2NBu^n_3 + 2CH_2{=}CHEt \quad (2)$$

The ability of the tetra-alkylammonium electrolyte to act as a base under our conditions is not surprising since reduction of CO_2 in a non-protic environment can lead to strongly basic conditions. Under such conditions these ions have been shown to undergo Hofmann degradation, as in equation (3).[11]

$$NEt_4^+ + B \rightarrow NEt_3 + HB^+ + C_2H_4 \qquad (3)$$

Electrocatalysed reduction of CO_2 can also be realized using Ru^{II}trpy complexes such as $Ru(trpy)(dppene)Cl^+$ [dppene = cis-1,2-bis(diphenylphosphino)ethylene]. Figure 1(b) shows the c.v. of this complex in MeCN–TBAH at a platinum disc working electrode. Of note is the single reduction process which by electrolysis is shown to involve two electrons. The irreversible nature of the reduction is due to reductively-induced loss of the Cl^- ligand which can be detected electrochemically after bulk electrolysis. The re-oxidation wave present in the c.v. is also a two electron process of the putative intermediate Ru(trpy)(dppene) formed upon reduction.

As seen in Figure 1(b) a small catalytic enhancement occurred at the onset of the two electron reduction wave when CO_2 was present in the solution. This enhancement is more pronounced at more negative potentials. Despite the small current enhancement the Ru complex was found to be a good CO_2 reduction catalyst at a potential of -1.4 V. Electrolysis of solutions 2.35 mM in complex (3.76×10^{-2} mmol) resulted in passage of 49.4 C in 1 h and subsequent analysis of the gases in equilibrium with the solution revealed the exclusive formation of CO (0.26 mM). Analysis of the solution proved negative for formate ion, but surprisingly, positive for NBu^n_3. In addition, after thoroughly purging the solution of CO_2 with a dry N_2 stream, acidification gave CO_2 in the gas phase. As determined from product analyses by g.c., the electrochemical stoicheiometry based upon CO, NBu^n_3, CO_3H^-, and electron count is that shown in equation (4).

$$NBu^n_4^+ + 2CO_2 + 2e^- \rightarrow NBu^n_3 + CH_2{=}CHEt + CO + CO_3H^- \qquad (4)$$
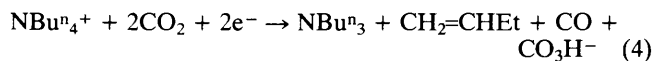
Neither CO_3^{2-} nor CO_3H^- are capable of deprotonating

tetra-alkylammonium salts under the conditions of the reaction. By inference the driving force for the Hofmann degradation in this case must be a highly basic, CO_2 containing intermediate which causes deprotonation of the tetrabutyl-ammonium ion to yield CO and OH^- (as CO_3H^-).

Our results have some important implications for the design of soluble transition metal complex catalysts for the reduction of CO_2. These are: (i) upon reduction the complexes lose a halide or pseudohalide ligand providing a potential binding site for CO_2; (ii) the polypyridyl ligands can act as electron acceptor sites at accessible potentials which undoubtedly plays a major role in the chemistry; (iii) selection of either CO or formate as the reduction product is possible depending on the nature of the catalyst.

References

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