Electrocatalytic Reduction of CO_2 to Oxalate by Ag^{II} and Pd^{II} Porphyrins

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New homogeneous catalysts, Ag^{II} and Pd^{II} metalloporphyrins, were found for the electrochemical reduction of CO_2 in CH_2Cl_2; oxalic acid and H_2 were detected as products.

The direct electrochemical reduction of CO_2 on various metal electrodes[1] has a large overpotential [more negative than -2 V *vs.* saturated calomel electrode (s.c.e.)], which thus requires a relatively high input of energy. Therefore, the search for electrocatalysts which mediate CO_2 reduction at lower potentials has become important. Indeed, several groups have recently demonstrated[2] such a catalytic effect using various transition metal complexes in which the metal is usually from the first row (mainly Co and Ni).

In this communication we describe the cathodic reduction of CO_2 in homogeneous solutions using for the first time Ag^{II} or Pd^{II} complexes of both 2,3,7,8,12,13,17,18,-octaethylporphyrin (OEP) and 5,10,15,20-tetraphenylporphyrin (TPP).[3] Cyclic voltammograms (c.v.s.) were carried out in a one compartment cell employing a glassy carbon (or Pt) button as the cathode, cylindrical platinum gauze as the anode, and a silver wire (+0.15 V *vs.* s.c.e.) as the reference electrode. Each of the metalloporphyrins studied was dissolved in 5 ml of dry CH_2Cl_2–0.2 M tetrabutylammonium fluoroborate (TBAF) and the c.v.s were run under Ar or CO_2. These c.v.s showed that only three of the four complexes studied, namely Ag^{II}(OEP), Pd^{II}(OEP), and Pd^{II}(TPP) displayed electrocatalytic activity when they were reduced in the presence of CO_2 (an example is shown in Figure 1). In comparison with two of the corresponding first-row transition metal complexes, Cu^{II}(TPP) and Ni^{II}(TPP) showed no catalytic activity. Clearly the combination of both metal and ligand in a given complex controls the extent of catalytic behaviour.

An H-type cell was employed in preparative electrolysis, in which the anolyte and catholyte were separated by a glass frit. The cathode was a polished glassy carbon plate (for the Ag^{II} complex) or platinum gauze (for the Pd^{II} complex), the anode a platinum sheet, and a polished silver wire functioned as the reference. Approximately 10 mg of either Ag(OEP) or Pd(OEP) were dissolved in ~ 40 ml of catholyte. A controlled potential of -1.50 and -1.65 V was applied respectively, and CO_2 was bubbled through the solutions throughout the electrolysis at atmospheric pressure. Current density was *ca.* 3 mA/cm^2, about 30 times greater than that of the background. The reaction was arbitrarily stopped after passing a total charge of 45—50 coulombs (~ 30 F/mol of catalyst!). In the case of Ag(OEP) the cathode was found to be coated with a thin film of silver mirror which is indicative of partial decomposition of the complex. This was also confirmed by its u.v.–visible spectra before and after the electrolysis. However, no palladium deposition was found in the case of Pd(OEP) although its partial decomposition was evidenced too by its visible spectrum. Gas chromatographic analysis [flame ionisation detector (f.i.d.)] was used to determine the composition of both the gases above the electrolysis solution

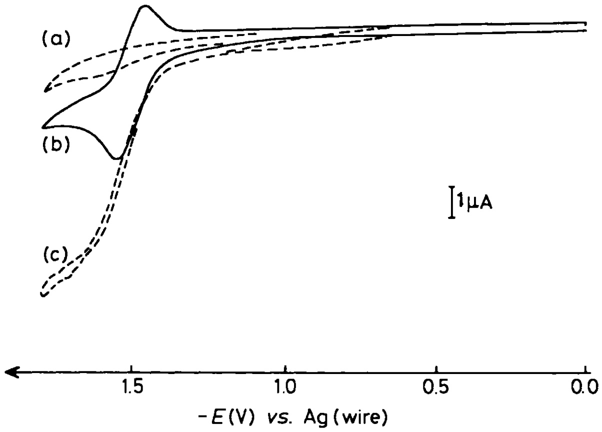

Figure 1. Cyclic voltammograms in CH_2Cl_2–0.1 M TBAF at glassy carbon cathode. Sweep rate 100 mV/s. (a) Background curve under argon. (b) A 5 ml solution containing 2.2 mg of Pd(OEP), under argon. (c) The same as in (b) but under CO_2.

and the products in the catholyte. Oxalic acid was the major product observed in either solution, and detected as its diester derivative (by esterification with diazomethane[4]). Surprisingly, only hydrogen was found in the gas phase (its source is not clear yet). No CO was detected by Fourier transform i.r. spectroscopy.

It is noteworthy that quite recently it was reported that complexes of Re[5] and Rh[6] showed electrocatalytic activity in aprotic homogeneous solutions towards a selective reduction of CO_2 to CO and HCOOH, respectively. Both these and our results indicate that complexes of the heavier transition metals could be selective catalysts for the electrochemical reduction of CO_2, and we are extending our efforts in this area.

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