Selective Production of Acetone in the Electrochemical Reduction of CO_2 Catalyzed by a Ru–Naphthyridine Complex

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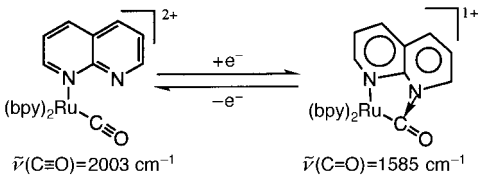
Electrochemical reduction of CO_2 with metal complexes is a feasible technique for the utilization of CO_2 as a C_1 source, though the reduction products usually have been limited to CO and/or HCOOH. Metal-catalyzed reductive disproportionation of CO_2 [Eq. (1)] proceeds through oxide transfer from a metal–CO_2 moiety to CO_2 [Eq. (2)] followed by reductive cleavage of the resultant metal–CO bond.

$$2\,CO_2 + 2\,e^- \longrightarrow CO + CO_3^{2-} \quad (1)$$

$$[M{-}CO_2]^{n+} + CO_2 \longrightarrow [M{-}CO]^{(n+2)+} + CO_3^{2-} \quad (2)$$

Acylation of the metal–CO bond would lead to a new methodology for carbon–carbon bond formation in the reduction of CO_2. Polypyridyl ruthenium carbonyl complexes such as $[Ru(bpy)_2(quinoline)(CO)]^{2+}$ and $[Ru(bpy)(terpyridine)(CO)]^{2+}$ (bpy = 2,2′-bipyridyl) work as catalysts for the reduction of CO_2 according to Equation (1),[1] and one-electron reduction of these complexes causes a bathochromic shift of their ν(CO) bands by about 30–40 cm^{-1}.[2] The mono-naphthyridine complex $[Ru(bpy)_2(napy)(CO)](PF_6)_2$ (**1**; napy = 1,8-naphthyridine) undergoes a pronounced bathochromic shift of the ν(CO) band ($\Delta\tilde{\nu} = 418\ cm^{-1}$) upon one-electron reduction due to nucleophilic attack of the non-bonded nitrogen atom of the monodentate napy ligand on the carbonyl carbon atom [Eq. (3)].[3]



(3)

Such a metallacyclization would suppress the reductive cleavage of the Ru–CO bond (CO evolution), and enable reduction of the CO group derived from CO_2. Here we report the first selective production of acetone in the electrochemical reduction of CO_2 catalyzed by $[Ru(bpy)(napy)_2(CO)_2](PF_6)_2$ (**2**) in the presence of $(CH_3)_4NBF_4$.

The two CO ligands of **2** are coordinated to Ru in *cis* positions, and the two napy moieties are linked to Ru in a monodentate manner, as depicted in the crystal structure (Figure 1).[4]

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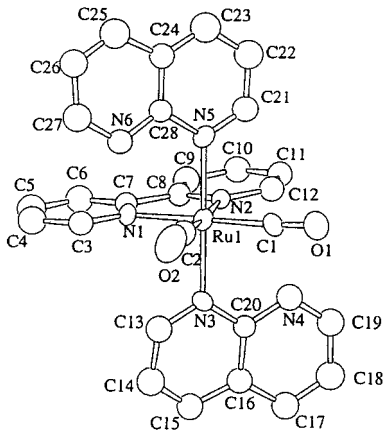

Figure 1. Molecular structure of the dication of **2** with atom labeling.

The cyclic voltammogram of **1** (0.1 mmol L^{-1}) in DMSO in the presence of $(CH_3)_4NBF_4$ (0.1 mol L^{-1}) under N_2 shows an irreversible cathodic wave at −1.40 V (all potentionals are given versus that of Ag/Ag^+) and three (quasi-)reversible redox couples at $E_{pc} = -1.63$, −1.80, and −2.02 V with peak separations (ΔE_{p-p}) of 60, 80 and 94 mV, respectively (Figure 2). The bis-napy complex **2** displays two irreversible

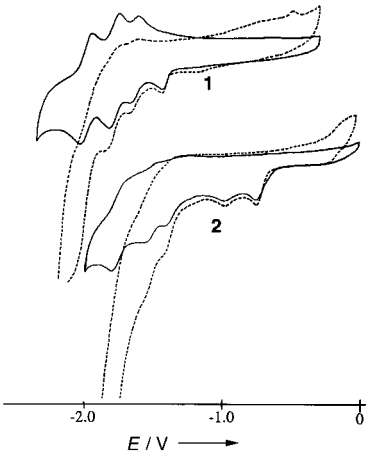

Figure 2. Cyclic voltammograms of **1** and **2** in the presence of $(CH_3)_4NBF_4$ under N_2 (——) and CO_2 (- - - -) in DMSO. The potential E is given in V versus Ag/Ag^+.

cathodic waves at $E_{pc} = -0.76$ and −0.98 V as well as three quasi-reversible couples at $E_{pc} = -1.44$, −1.58, and −1.94 V with $\Delta E_{p-p} = 80$ mV under the same conditions. One irreversible cathodic wave of **1** ($E_{pc} = -1.42$ V) and two irreversible waves of **2** ($E_{pc} = -0.76$ and −0.98 V) result from reduction of the napy ligands followed by formation of the Ru-C(O)-N-N ring [Eq. (3)]. Introduction of CO_2 to the solutions of **1** and **2** in DMSO causes strong catalytic currents due to the reduction of CO_2 (Figure 2), since electrochemical reduction of CO_2 takes place at potentials more negative than −2.4 V in the absence of these complexes. It is noteworthy that the reduction of CO_2 by **2** occurs at potentials more negative than −1.4 V, while the threshold potential of the CO_2 reduction by **1** is close to −2.0 V.

In agreement with Equation (1), only CO and Li_2CO_3 were produced in the controlled potential electrolysis of **2**

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(0.6 mmol L^{-1}) at -1.65 V with a glassy carbon (GC) electrode (4 cm^2) in CO_2-saturated DMSO (30 mL)[5] containing $LiBF_4$ (0.1 mol L^{-1}) as electrolyte. On the other hand, when $(CH_3)_4NBF_4$ was used as an electrolyte under otherwise similar conditions, acetone was selectively generated with a traces of CO. The amounts of these products increased with the electricity, as shown in Figure 3. Besides acetone and CO,

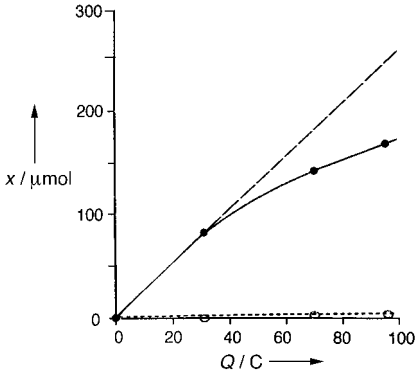

Figure 3. The amounts x of acetone (●) and CO (○) generated in the electrochemical reduction of CO_2 catalyzed by **2** in the presence of $(CH_3)_4NBF_4$ in DMSO at -1.60 V. The dashed line represents the theroretical amount of acetone expected based on Equation (4).

$(CH_3)_3N$ and $\{(CH_3)_4N\}_2CO_3$ were the only other products detected in the solution. Thus, $(CH_3)_4N^+$ works not only as an electrolyte, but also as a methylation reagent for the catalytic generation of acetone in the electrochemical reduction of CO_2 catalyzed by **2** [Eq. (4)].

$$2\,CO_2 + 4\,e^- + 2(CH_3)_4N^+ \longrightarrow CH_3C(O)CH_3 + CO_3^{2-} + 2\,(CH_3)_3N \qquad (4)$$

Based on the stoichiometry of Equation (4), the current efficiency of acetone was 70% at 100 °C (turnover number 8.5) and that of CO was less than 1%. This first selective formation of acetone in the electrochemical reduction of CO_2 [Eq. (4)] is associated with the suppression of reductive cleavage of the Ru–CO bond [Eq. (1)] by the metallacyclization shown in Equation (3).[6] Indeed, the current densities of the GC electrodes in the reduction of CO_2 catalyzed by **2** were 5 and 0.25 mA cm^{-2} in the presence of $(CH_3)_4NBF_4$ [Eq. (4)][7] and $LiBF_4$ [Eq. (1)], respectively. Moreover, the electrolysis potential is of fundamental importance for the catalytic generation of acetone, since acetone undergoes irreversible reduction at potentials of -2.0 V on GC electrodes in DMSO. Therefore, from the viewpoints of the threshold potential for the reduction of CO_2 (Figure 2), **1** is not a suitable catalyst for the reduction shown in Equation (4) even though CO evolution is depressed by the metallacyclization reaction of Equation (3).[8]

Experimental Section

To a solution of $RuCl_3 \cdot 3\,H_2O$ (1 mmol) in ethanol (50 mL) was added bpy (1 mmol), and the solution was heated under reflux for 2 h. Then Et_3N (0.5 mL) and napy (3 mmol) were added, and the solution was heated under reflux for 2 h. The reaction mixture was concentrated to about 5 mL. Addition of $NaBF_4$ (2 mmol) in H_2O resulted in precipitation of purple $[Ru(bpy)(napy)_2Cl]BF_4$ in 80% yield. A suspension of $[Ru(bpy)(napy)_2Cl]BF_4$ in ethanol was heated at 60 °C under CO (40 atm) for 15 h. Concentration of the solution and treatment with an aqueous solution of $NaBF_4$ gave $[Ru(bpy)(napy)_2(CO)_2](BF_4)_2$ as a yellow powder in 70% yield. Elemental analysis calcd for $C_{28}H_{20}N_6B_2F_8Ru$: C 44.98, H 2.68, N 11.24; found: C 44.83, H 2.39, N 11.24; IR: $\tilde{\nu} = 2077$, 2027 cm^{-1} (CO).

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[4] a) Crystal data for **1**: monoclinic, $P2_1/n$, $a = 10.696(2)$, $b = 14.989(3)$, $c = 18.395(2)$ Å, $\beta = 99.58(1)°$, $V = 2907.7(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.707$ g cm^{-3}, $20.2 < 2\theta < 23.6°$, $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å); of 7296 reflections observed, 6936 were independent. The structure was solved by direct methods (SAPI91) and refined against $|F|$ with 2230 reflections ($I > 3.0\sigma(I)$) and 234 parameters; $R = 0.071$ and $R_w = 0.060$. b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101753. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[5] The concentration of residual water in the DMSO was 21 μmol L^{-1}.

[6] The electrochemical reduction of CO_2 also took place in CH_3CN, though in this case CO_3^{2-} is likely to deposit on the electrode. An orange solution obtained upon concentration of the electrolyzed solution of **2** in CH_3CN became yellow after exposure to air. Appearance of the two ν(CO) bands typical of **2** in the IR spectra of the resultant yellow solution strongly indicates that the reduced form of **2** is the stable catalyst in the formation of acetone.

[7] An initial current density of 5 mA cm^{-2} dropped to about one-third at 100 C due to consumption of $(CH_3)_4NBF_4$. Renewed addition of electrolyte to the solution resulted in almost complete recovery of the initial current density.

[8] Only a small amount of isopropyl alcohol was detected (current efficiency of about 10%) in the electrochemical reduction of CO_2 catalyzed by **1** at -2.00 V in DMSO in the presence of $(CH_3)_4NBF_4$.

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