CHEMISTRY LETTERS, pp. 955-958, 1993.

Carbon-Carbon Bond Formation in Multi-electron Reduction of Carbon Dioxide Catalyzed by $[Ru(bpy)(trpy)(CO)]^{2+}$ (bpy = 2,2'-bipyridine; trpy = 2,2':6',2"-terpyridine)

Hirotaka NAGAO, Tetsunori MIZUKAWA, and Koji TANAKA*
Institute for Molecular Science, Myodaiji, Okazaki 444

Controlled potential electrolysis of $[Ru(bpy)(trpy)(CO)]^{2+}$ (bpy=2,2'-bipyridine; trpy = 2,2':6',2"-terpyridine) at -1.70 V *vs.* Ag|Ag^+ in CO_2-saturated C_2H_5OH/H_2O (8:2 v/v) at -20 °C produced not only HCOOH and CO but also HC(O)H, CH_3OH, H(O)CCOOH, and $HOCH_2COOH$.

Much attention has been paid to electro- and photochemical CO_2 reduction catalyzed by transition metal complexes.[1)] The reduction products in those homogeneous reactions, however, have been limited to CO and HCOOH so far, and four- and six-electron reduction products have not been obtained. The direct conversion of CO_2 to organic molecules other than HCOOH, therefore, is highly desired in the viewpoint of the utilization of CO_2 as C1 resources. We have reported that $[Ru(bpy)_2(CO)_2]^{2+}$(**1**), $[Ru(bpy)_2(CO)(C(O)OH)]^+$, and $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ exist as equilibrium mixtures in aqueous conditions.[2)] Those complexes function as the precursors for the CO and HCOOH formation and the CO_2 adduct, respectively, in the catalytic cycle of the electro- and photochemical CO_2 reductions.[3)] The difficulty in the multi-electron reduction of CO_2 by **1** may be ascribed to the dissociation of CO upon the reduction of **1**. Suppression of such dissociation of CO from metal-carbonyl complexes playing the role in the precursor of CO may, therefore, lead to reduction of the carbonyl ligand. This paper reports the multi-electron reduction of CO_2 catalyzed by $[Ru(bpy)(trpy)(CO)]^{2+}$ (**2**).

The cyclic voltammogram (CV) of **1** shows an irreversible two-electron cathodic wave (E_{cp}= -1.29 V *vs.* Ag|Ag^+)[3)] (a solid line in Fig. 1a), and that of **2** displays stepwise one-electron reversible couple (E_{cp} and E_{ap}=-1.36 and -1.29 V) and an irreversible cathodic wave (E_{cp}=

-1.68 V) in CH_3CN at 20 °C(a solid line in Fig. 1b).[4] The redox behavior of **1** was not changed even at -40 °C. On the other hand, the CV of **2** at -20 °C clearly showed the anodic wave (E_{ap}=-1.57 V) coupled with the -1.68 V cathodic one in addition to the reversible redox couple at $E_{1/2}$=-1.33 V. These results indicate that electrochemical reduction of **1** is followed by decomposition due to the liberation of CO[3] even at -40 °C, while the two-electron reduced form of **2**, $[Ru(bpy)(trpy)(CO)]^0$, is fairly stable at -20 °C. As similar to **1**, **2** also has an ability to catalyze the electrochemical reduction of CO_2, since both **1** and **2** show similar catalytic cathodic currents at potentials more negative than -1.6 V in CH_3CN under CO_2 atmosphere at 20°C (dotted lines in Fig. 1a and b).

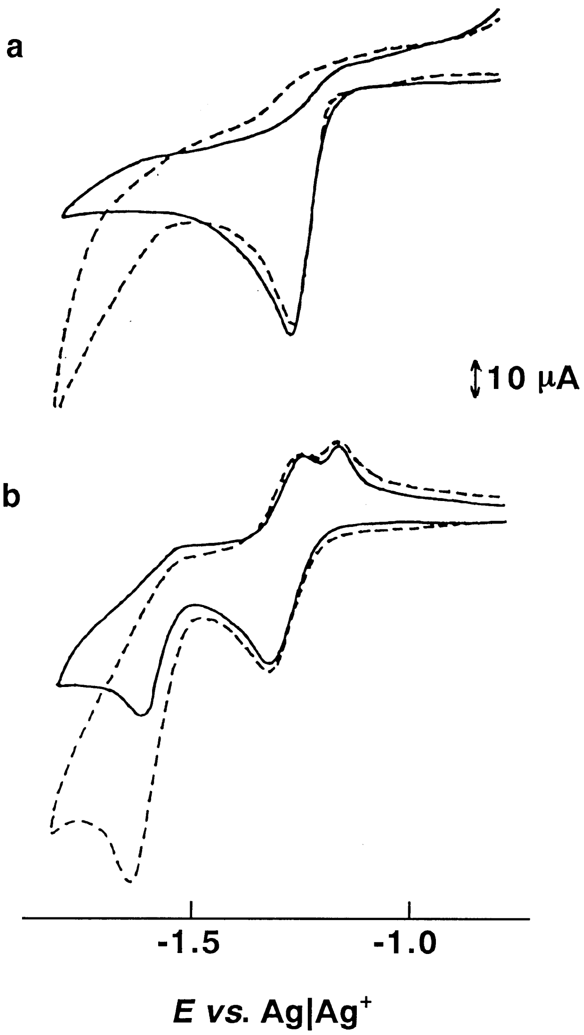

Fig. 1. Cyclic voltammograms of **1** (a) and **2** (b) in CH_3CN containing Bu_4NBF_4 (0.1 mol dm^{-3}) as a supporting electrolyte under N_2 (solid line) and CO_2 (dotted line). dE/dt=100 mV/s. working electrode; glassy carbon.

The controlled potential electrolysis of **2** in C_2H_5OH/H_2O (8:2 v/v) at -1.70 V under CO_2 atmosphere produced a trace amount of CH_3OH with current efficiency (η) of 0.3% together with CO, HCOOH, and H_2 (35, 20 and 20%, respectively) at 20 °C.[5] The latter three were also produced in the electrochemical CO_2 reduction catalyzed by **1** under similar electrolysis conditions. The efficiency for the multi-electron reduction of CO_2 is greatly improved when the CO_2 reduction by **2** was conducted under the controlled potential electrolysis at -1.75 V in the same solvent at -20 °C. As depicted in Fig. 2, not only CO, HCOOH, HC(O)H, and CH_3OH but also C2 compounds such as $HOCH_2COOH$ and H(O)CCOOH are generated in the electrolysis.[5,6] Furthermore, reoxidation of

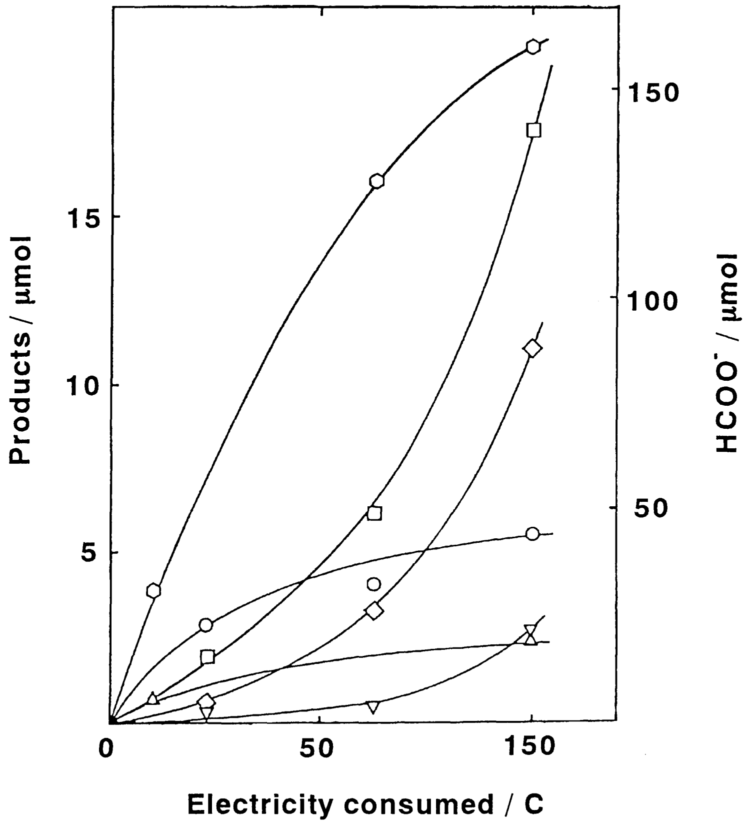

Fig. 2. Plots of the amounts of CO(△), $HCOO^-$(□), HC(O)H (◇), CH_3OH(▽), $H(O)CCOO^-$(○), and $HOCH_2COO^-$(○) *vs.* the electricity consumed in the reduction of CO_2 by **2** (2.5×10^{-5} mol) under the controlled potential electrolysis at -1.75 V *vs.* Ag|Ag^+ in C_2H_5OH/H_2O(8:2 v/v) at -20 °C.5)

the final solution (after 100 C was passed) at -0.5 V almost regenerated the electronic absorption spectrum of the initial solution.7) This observation strongly suggests that **2** exists stably during the electrolysis. On the other hand, the electrochemical reduction of CO_2 by **1** under similar conditions at -20 °C produced only CO and HCOOH as similar to the electrolysis at 20 °C, and neither CH_3OH, $HOCH_2$-COOH, H(O)CCOOH, nor HC(O)H was formed at all. The precursors for the HCOOH and CO formation in the reduction of CO_2 by **2** may be $[Ru(bpy)(trpy)(C(O)OH)]^+$ and [Ru(bpy)(trpy)(CO)] from analogy with that by **1**3) The multi-electron reduction of CO_2 by **2** at -20 °C may be caused by stability of the two-electron reduced form and successive protonation of the carbonyl ligand affording $[Ru(bpy)(trpy)(C(O)H)]^+$ and $[Ru(bpy)(trpy)(CH_2OH)]^+$ as the precursors for the HC(O)H and CH_3OH formation. Alternatively, carboxylation of $[Ru(bpy)(trpy)(C(O)H)]^+$ and $[Ru(bpy)(trpy)(CH_2OH)]^+$ under the electrolysis conditions is expected to give C2 compounds such as H(O)CCOOH and $HOCH_2COOH$ in Fig. 2. Thus, formation of not only four-electron reduction products (HC(O)H and H(O)CCOOH) but also six-electron products (CH_3OH and $HOCH_2COOH$) may be reasonably explained by the presence of $[Ru(bpy)(trpy)(C(O)H)]^+$ and $[Ru(bpy)(trpy)(CH_2OH)]^+$ in the catalytic cycle of the electrochemical CO_2 reduction by **2** at -20 °C. It is, therefore, concluded that the distinct difference in the ability of **1** and **2** toward the multi-electron reduction of CO_2 at -20 °C results from the stability of $[Ru(bpy)_2(CO)_2]^0$ and $[Ru(bpy)(trpy)(CO)]^0$ at that temperature.

References

1) J.-C. Tsai and K. M. Nicholas, *J. Am. Chem. Soc.*, **114**, 5117(1992); C. Arana, S. Yan, M. Keshavarz, K. T. Potts, and H. D. Abruna, *Inorg. Chem.*, **31**, 3690(1992); E. Kimura, X. Bu, M. Shionoya, S. Wada, and S. Maruyama, *ibid.*, **31**, 4542(1992); M. R. M. Bruce, E. Megehee, B. P. Sullivan, H. H. Thorp, T. R. O'Toole, A. Downard, J. R. Pugh, and T. J. Meyer, *ibid.*, **31**, 4864(1992); P. Christensen, A. Hamnett, A. V. G. Muir, and J. A.Timney, *J. Chem. Soc., Dalton Trans*, **1992**, 1455; K. S. Ratliff, R. E. Lentz, and C. P. Kubiak, *Organometallics* , **11**, 1986(1992); E. Graf and W. Leitner, *J. Chem. Soc., Chem. Commun.*, **1992**, 623; D. L. Dubois, A. Miedaner, and R. C. Haltiwanger, *J. Am. Chem. Soc.*, **113**, 8753(1991); T. Atoguchi, A. Aramata, A. Kazusaka, and M. Enyo, *J. Chem. Soc., Chem. Commun.*, **1991**, 156; J. C. Tsai, M. A. Khan, and K. M. Nicholas, *Organometallics* , **10**, 29(1991); E. Fujita, C. Creutz, N. Sutin, D. J. Szalda, *J. Am. Chem. Soc.*, **113**, 343(1991); J. R. Pugh, M. R. M. Bruce, B. P. Sullivan, T. J. Meyer, *Inorg. Chem.*, **30**, 86(1990) and references therein.

2) H. Ishida, K. Tanaka, M. Morimoto, and T. Tanaka, *Organometallics* , **5**, 724(1986); H. Tanaka, H. Nagao, S.-M. Peng, and K. Tanaka, *ibid.*, **11**, 1450(1992).

3) H. Ishida, K. Tanaka, and T. Tanaka, *Organometallics* , **5**, 181(1987).

4) The oxidation wave at around -1.2 V presumable resulted from decomposition of the two-electron reduced form of **2** since this wave was not observed when the potential returned at -1.5 V.

5) The reaction products were analyzed by GC, GC-Mass, LC, and Isotachophoretic Analyzer. The amounts of CO, H_2, HCHO, and CH_3OH were determined by GC, and that of $HCOO^-$ by Isotachophoretic Analyzer. The analyses of H(O)CCOOH and $HOCH_2COOH$ by GC and GC-Mass were conducted after conversion to $H(O)CCOOCH_3$ and $HOCH_2COOCH_3$ by treatment of the crude products with CH_2N_2.

6) The controlled potential electrolysis at -1.75 V in the absence of **2** produced neither CO, HCOOH, HCHO, CH_3OH, H(O)CCOOH nor $HOCH_2COOH$ at all under the similar conditions at -20 °C.

7) The regeneration of **2** after reoxidation of the final solution at -0.5 V was also confirmed by the IR spectrum of the reaction residue obtained by evaporation of the solvent.

(Received March 10,1993)