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Oxalate Formation in Electrochemical CO_2 Reduction Catalyzed by Rhodium-Sulfur Cluster

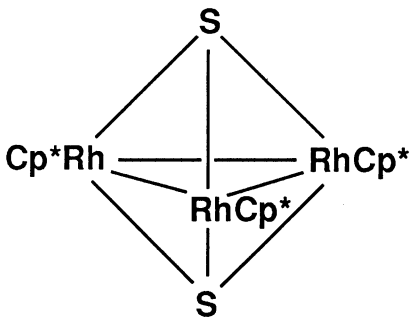
Yoshinori KUSHI, Hirotaka NAGAO, Takanori NISHIOKA, Kiyoshi ISOBE, and Koji TANAKA*

Department of Structural Science, The Graduate University for Advanced Studies,

Institute for Molecular Science, Myodaiji, Okazaki 444

Electrochemical reduction of CO_2 catalyzed by a triangular rhodium complex $[(RhCp^*)_3(\mu_3\text{-}S)_2]^{2+}$ selectively produced formate and oxalate in the presence of Bu_4NBF_4 and $LiBF_4$, respectively, under the controlled potential electrolysis at -1.50 V (*vs.* SCE) in CO_2-saturated CH_3CN. A solution IR spectrum evidenced the adduct formation between $[(RhCp^*)_3(\mu_3\text{-}S)_2]^0$ and CO_2 as the possible precursor for the oxalate formation.

Direct electrochemical reduction of CO_2 takes place at potentials more negative than -2.0 V *vs.* SCE under anhydrous conditions.[1] To reduce the high overpotential for the CO_2 reduction, much efforts have been paid to search for metal complexes to mediate CO_2 reduction at less negative potentials. A variety of transition metal complexes have been shown to catalyze electrochemical CO_2 reduction producing CO and/or $HCOO^-$.[2] Metal-η^1-CO_2 intermediates are generally believed as the precursors for those products,[3] and the molecular structures of Rh-,[4] Co-,[5] and Ru-η^1-CO_2 complexes[6] have been elucidated so far in this connection. On the other hand, a CO_2 adduct bonded on bridging sulfur of $[Mo_2Fe_6S_8(SEt)_9]^{5-}$ is proposed as a reaction intermediate in CO_2 fixation to thioesters affording α-keto acids.[7] Thus, not only low valent metals but also electron rich sulfur ligands are the possible sites for the activation of CO_2 by metal-sulfur clusters. This paper describes the first



Sturucture of rhodium cluster $[\mathbf{1}]^{2+}$

successful oxalate generation in a high yield in electrochemical CO_2 reduction catalyzed by $[(RhCp^*)_3(\mu_3\text{-}S)_2]^{2+}$ ($[\mathbf{1}]^{2+}$)[8] as a homogeneous catalyst.

The cyclic voltammogram of a BPh_4 salt of $[\mathbf{1}]^{2+}$ showed two reversible $[\mathbf{1}]^{2+/+}$ and $[\mathbf{1}]^{+/0}$ redox couples at $E_{1/2}$= -0.52 and -0.91 V *vs.* SCE in CH_3CN under N_2 atmosphere (Solid line in Fig. 1(a)). Introduction of CO_2 into the solution by bubbling brought about a slight increase in cathodic current at potentials more negative than -1.20 V (Dotted line in Fig. 1(a)), though the $[\mathbf{1}]^{2+/+}$ and $[\mathbf{1}]^{+/0}$ redox waves were essentially unchanged between N_2 and CO_2 atmospheres at 20 °C. On the other hand, when $[\mathbf{1}]^{2+}$ existing on the electrode is reduced to $[\mathbf{1}]^0$ by applying a potential of -1.50 V to the solution for 3 min under CO_2 atmosphere at -5 °C, a new anodic wave appeared at -0.73 V at the sacrifice of the anodic peak current of the $[\mathbf{1}]^{0/+}$ couple at -0.87 V in the following potential sweep between -1.50 and -0.60 V at 0.1 V/s (Dotted line in Fig. 1(b)). This observation is an indication of a strong interaction between $[\mathbf{1}]^0$ and CO_2.

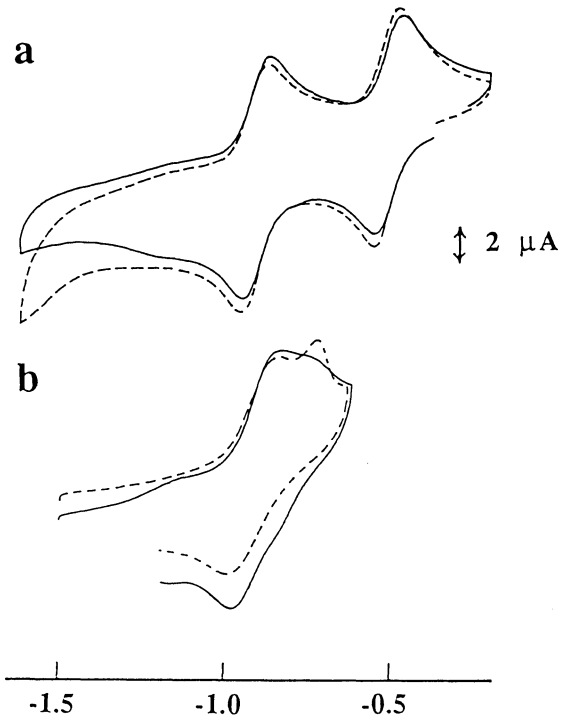


Fig. 1. Cyclic voltammograms of $[\mathbf{1}]^{2+}$ in the presence of Me_4NBF_4 in CH_3CN under N_2 (—) and CO_2 (---) atmospheres at room temperature (a), and after cathodic polarization at -1.50 V for 3 min at -5 °C (b) ; dE/dt = 0.1 V/s.

The controlled potential electrolysis at -1.50 V of a CH_3CN solution (15 cm^3) containing $[\mathbf{1}](BPh_4)_2$ (15 μmol) and Bu_4NBF_4 (1.5 mmol) with a glassy carbon plate (1.0 x 1.5 cm^2) under CO_2 atmosphere produced $HCOO^-$ with a current efficiency of 60%. The concomitant generation of the corresponding amounts of $CH_3CH_2CH{=}CH_2$ and Bu_3N in the solution indicates that Bu_4N^+ functions as a proton source in the electrochemical CO_2 reduction by $[\mathbf{1}]^{2+}$ (eq. 1).[9] Exposure of the final electrolyte solution (after 60 C passed in the electrolysis) to air resulted in complete regeneration of the electronic absorption spectrum of $[\mathbf{1}]^{2+}$ (λmax = 295 nm) in CH_3CN. Thus, $[\mathbf{1}]^{2+}$ works stably as the catalyst without undergoing a fragmentation reaction during the electrochemical CO_2 reduction in eq.1.

$$CO_2 + Bu_4N^+ + 2e^- \longrightarrow HCOO^- + CH_3CH_2CH{=}CH_2 + Bu_3N \quad (1)$$

A similar electrolysis using $LiBF_4$ as an electrolyte to avoid the participation of Bu_4N^+ in the electrochemical CO_2 reduction by $[\mathbf{1}]^{2+}$ in CH_3CN also smoothly proceeded and selectively produced $Li_2(C_2O_4)$[10] as a white precipitate under otherwise the same reaction conditions. Thus, in the absence of proton donor, $[\mathbf{1}]^{2+}$ catalyzes the electrochemical reduction of CO_2 affording oxalate (eq. 2),

$$2CO_2 + 2e^- \longrightarrow {}^-OOCCOO^- \quad (2)$$

since a glassy carbon plate has no ability to reduce CO_2 at -1.50 V in CH_3CN. The current efficiency for oxalate calculated from $Li_2(C_2O_4)$ recovered after the electrolysis was 60%.

As expected from the $E°(CO_2/CO_2^-)$ value of -2.21 V, direct electron transfer from $[\mathbf{1}]^0$ to CO_2 in CH_3CN is thermodynamically unfavorable. Oxalate generation in eq. 2, therefore, results from an activation of CO_2 on $[\mathbf{1}]^0$. Indeed, a solution IR spectrum of $[\mathbf{1}](BPh_4)_2$ in CO_2-saturated CD_3CN evidenced the formation of not only oxalate but also the CO_2 adduct under the electrolysis at -1.50 V; three new bands gradually appeared at 1680, 1633 and 1605 cm^{-1} when the potential was applied to the solution, and grew in intensities with time. The 1680 and 1605 cm^{-1} bands completely disappeared upon the reoxidation of the solution at 0.3 V, while the 1633 cm^{-1} band assigned to oxalate remained after the reoxidation. Thus, the former two bands are reasonably associated with CO_2 bonded to $[\mathbf{1}]^0$. Although the binding sites of CO_2 to $[\mathbf{1}]^0$ are not clear at present, the observation of two $\nu(CO_2)$ bands in the IR spectrum of $[\mathbf{1}]^0$ under CO_2 may have the fundamental significance for the generation of oxalate in eq. 2. Each rhodium linked by Cp^*, two Rh, and bridging S in $[\mathbf{1}]^{2+}$ apparently has no vacant site to interact with CO_2. On the other hand, one of the metal-metal bond of an analogous triangular iridium complex, $[(IrCp^*)_3(\mu_3\text{-}S)_2]^{2+}$, is fissioned upon two electron reduction.[11] If the same configurational change takes places also in $[\mathbf{1}]^0$, the resulting coordinatively unsaturated Rh atoms may undergo an electrophilic attack of two CO_2 molecules to form the 1:2 adduct. Alternatively, if one of the Rh-S bond of $[\mathbf{1}]^{2+}$ is weakened upon two-electron reduction in contrast to $[(IrCp^*)_3(\mu_3\text{-}S)_2]^0$, two CO_2 molecules may be linked by S and Rh of $[\mathbf{1}]^0$. The catalytic formation of oxalate in eq. 2, therefore, may be attributed to the coupling reaction of two CO_2 molecules trapped on either two Rh or S and Rh in $[\mathbf{1}]^0$. Although oxalate formation has been reported in the electrochemical reduction of CO_2 catalyzed by Pd(oep) (oep = 2, 3, 7, 8, 12, 13, 17, 18, -octa-ethylporphyrin) in CH_2Cl_2 at -1.50 V, neither the

current efficiency nor details of the reaction is described.[12] The present electrochemical CO_2 reduction catalyzed by $[\mathbf{1}]^{2+}$, therefore, is the first successful oxalate formation in a high current efficiency under homogeneous reaction conditions. The elucidation of the reaction mechanism including the reaction site of $[\mathbf{1}]^0$ in eq. 2 is now in progress.

References

1) J. Desilvestro and S. Pons, *J. Electroanal. Chem.*, **267**, 207 (1989); C. Amatore and J. -M. Saveant, *J. Am. Chem. Soc.*, **103**, 5021 (1981); J. -C. Gressin, D. Michelet, L. Nadjo, and J. -M. Saveant, *Nouv. J. Chim.*, **3**, 545 (1979).
2) A. Deronzier and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, **1994**, 189; T. Yoshida, K. Tsutsumida, S. Teratani, K. Yasufuku, and M. Kaneko, *J. Chem. Soc., Chem. Commun.*, **1993**, 631; 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, and D. J. Szalda, *J. Am. Chem. Soc.*, **113**, 343 (1991); J. R. Pugh, M. R. M. Bruce, B. P. Sullivan, and T. J. Meyer, *Inorg. Chem.*, **30**, 86 (1990) and references therein.
3) H. Nagao, T. Mizukawa, and K. Tanaka, *Inorg. Chem.*, **33**, 3415 (1994).
4) J. C. Calabrese, T. Herskovitz, and J. B. Kinney, *J. Am. Chem. Soc.*, **105**, 5914 (1983).
5) S. Gambarotta, F. Arena, C. Floriani, and P. F. Zanazzi, *J. Am. Chem. Soc.*, **104**, 5082 (1982).
6) H. Tanaka, H. Nagao, and K. Tanaka, *Inorg. Chem.*, **31**, 1971 (1992).
7) N. Komeda, H. Nagao, T. Matsui, G. Adachi, and K. Tanaka, *J. Am. Chem. Soc.*, **114**, 3625 (1992).
8) T. Nishioka and K. Isobe, *Chem. Lett.*, **1994**, 1661.
9) M. Tezuka, T. Yajima, A. Tsutuya, Y. Matsumoto, Y. Uchida, and M. Hidai, *J. Am. Chem. Soc.*, **104**, 6835 (1982); M. Nakazawa, U. Mizobe, Y. Matsumoto, Y. Uchida, M. Tezuka, and M. Hidai, *Bull. Chem. Soc. Jpn.*, **59**, 809 (1986).
10) Oxalate was identified as dimethyl oxalate by GC-Mass after treatments of the crude products with CH_2N_2 in diethyl ether, and the quantitative analysis was conducted by a use of isotachophoresis.
11) A. Venturelli and T. B. Rauchfuss, *J. Am. Chem. Soc.*, **116**, 4824 (1994).
12) J. Y. Becker, B. Vainas, R. Eger, and L. Kaufman, *J. Chem. Soc., Chem. Commun.*, **1985**, 1471.

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