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

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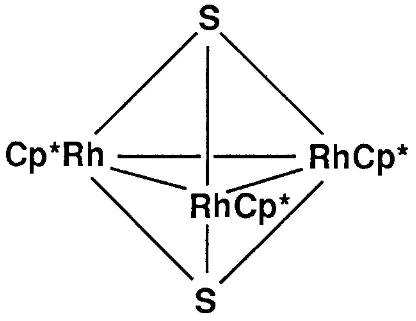
Electrochemical reduction of CO_2 catalyzed by a triangular rhodium complex $[(RhC_p^*)_3(\mu_3\text{-}S)_2]^{2+}$ selectively produced formate and oxalate in the presence of Bu_4NBF_4 and $LiBF_4$, respectively, under the controlled potential electrolysis at -1.50 V (*vs.* SCE) in CO_2-saturated CH_3CN. A solution IR spectrum evidenced the adduct formation between $[(RhC_p^*)_3(\mu_3\text{-}S)_2]^0$ 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 complexes6) 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 $[1]^{2+}$

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.

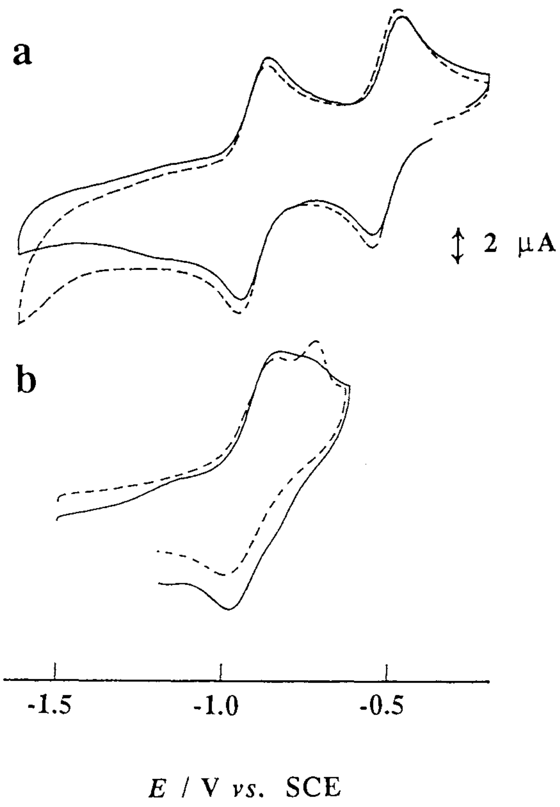


Fig. 1. Cyclic voltammograms of $[\mathbf{1}]^{2+}$ in the presence of Me_4NBF_4 in CH_3CN under N_2 (—) and CO_2 (---) atmospheres at room temperature (a), and after cathodic polarization at -1.50 V for 3 min at -5 °C (b) ; d*E* / dt = 0.1 V/s.

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, $[(IrC_p{}^*)_3(\mu_3\text{-}S)_2]^{2+}$, 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 $[(IrC_p{}^*)_3(\mu_3\text{-}S)_2]^0$, 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.

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