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Electrochemical Carboxylation of Ketones $RCOCH_2R'$ Coupled with CO_2 Reduction by $[Ru(bpy)_2(CO)_2]^{2+}$

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Electrochemical carboxylation of $PhCOCH_3$ and $C_6H_{10}(O)$ coupled with CO_2 reduction by $[Ru(bpy)_2(CO)_2]^{2+}$ was carried out in CO_2-saturated dry CH_3CN. CO_2 ligated on the ruthenium atom is reduced to $HCOO^-$ or CO upon the electrochemical reduction of the complex, where $PhCOCH_3$ and $C_6H_{10}(O)$ function as a proton source, and the resultant carbanions react with CO_2 to afford the corresponding ketoacids, catalytically.

Recently much attention has been paid to the electrochemical CO_2 reduction catalyzed by transition metal complexes[1)] though most of the reaction products are limited to CO and/or $HCOO^-$.[2)] Electrochemical production of carboxylic acids by the reaction of organic halides with CO_2, therefore, has been conducted in the presence of catalytic amounts of Ni[3)] and Pd[4)] complexes under galvanostatic conditions. In viewpoints of utilization of CO_2, however, the electrochemical carboxylation accompanied by a carbon-hydrogen bond cleavage may be more important than that by a carbon-halogen bond cleavage. Nitrite ion ligated on transition metals is subject to dissimilatory and assimilatory reductions affording N_2 [5)] or N_2O [6)] and NH_3,[5,7)] respectively. By taking advantage of the strong basicity of NO_2^- coordinated to the reduced species of $[Fe_4S_4(SPh)_4]^{2-}$, the first catalytic carboxylation of $PhCOCH_3$ has been succeeded under the controlled potential electrolysis of CO_2-saturated CH_3CN containing $[Fe_4S_4(SPh)_4]^{2-}$, NO_2^-, and $PhCOCH_3$.[8)] The electrochemical carboxylation coupled with NO_2^- reduction catalyzed by 2,2'-bipyrizylruthenium complex is also of interest since ruthenium complexes have been elucidated to show high catalytic activity toward the reductions not only of NO_2^- 5) but also CO_2.9) This study has revealed that $[Ru(bpy)_2(CO)_2]^{2+}$ has an ability of catalyzing the electrochemical carboxylation of $PhCOCH_3$ and $C_6H_{10}(O)$ even in the absence of NO_2^- in CO_2-saturated CH_3CN.

Nitrite ion selectively undergoes a dissimilatory reduction to afford N_2 (Eq. 1) under the controlled potential

$$2NO_2^- + 8H^+ + 6e^- \longrightarrow N_2 + 4H_2O \qquad (1)$$

electrolysis of CO_2-saturated dry CH_3CN (17 cm^3) containing $[Ru(bpy)_2(CO)_2]^{2+}$ (16.5 µmol), Et_4NNO_2 (0.52 mmol), $PhCOCH_3$ (14.1 mmol), Bu_4NBr (1.65 mmol), and molecular sieves 3A as a dehydration agent at -1.40 V vs. SCE. At the same time, $PhCOCH_2COO^-$, $HCOO^-$, and CO are formed catalytically (Fig. 1). The latter two apparently result from the reduction of CO_2 (Eqs. 2 and 3). This result

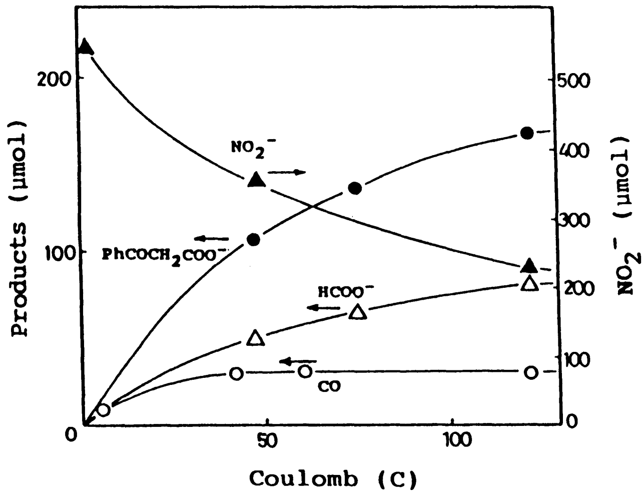


Fig. 1. Controlled potential electrolysis of CO_2-saturated CH_3CN containing $[Ru(bpy)_2(CO)_2]$-$(PF_6)_2$, Et_4NNO_2, $PhCOCH_3$, and Bu_4NBr in the presence of molecular sieves 3A at -1.40 V vs. SCE.

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O \qquad (2)$$

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH \qquad (3)$$

suggests that $PhCOCH_3$ functions as a proton source in the reduction not only of NO_2^- but also of CO_2, and the main product $PhCOCH_2COO^-$ is produced by the reaction of the resultant $PhCOCH_2^-$ with CO_2. Thus, $[Ru(bpy)_2(CO)_2]^{2-}$ can catalyze the electrochemical carboxylation coupled with CO_2 reduction in contrast to $[Fe_4S_4(SPh)_4]^{2-}$, which has no ability of catalyzing CO_2 reduction under the same reaction conditions. This is consistent with the fact that the controlled potential electrolysis of CO_2-saturated CH_3CN (17 cm^3) containing

$[Ru(bpy)_2(CO)_2]^{2+}$ (19.3 μmol), $PhCOCH_3$ (20.6 mmol) and Bu_4NBr (1.94 mmol) at -1.40 V vs. SCE catalytically produced not only $HCOO^-$ and CO but also $PhCOCH_2COO^-$ (Fig. 2). Similarly, when CO_2 reduction was conducted in the presence of $C_6H_{10}(O)$ in place of $PhCOCH_3$ unless otherwise the same reaction conditions, cyclohexanone-2-carboxylic acid was catalytically produced accompanied by the formation of $HCOO^-$ and CO. On the other hand, the electrolysis of $[Ru(bpy)_2(CO)_2]^{2-}$ in CO_2-saturated dry CH_3CN in the absence of either $PhCOCH_3$ or $C_6H_{10}(O)$ resulted in a decomposition of the complex with evolving a trace amount of CO.[10)]

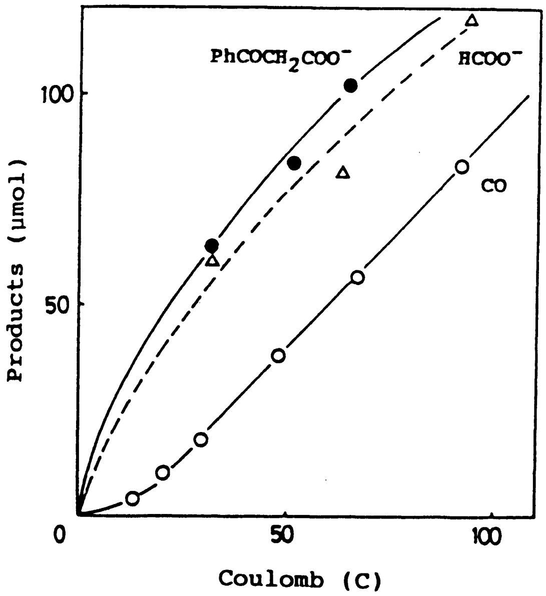
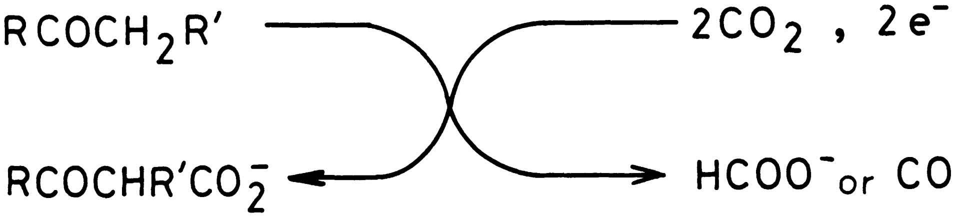


Fig. 2. Controlled potential electrolysis of CO_2-saturated CH_3CN containing $[Ru(bpy)_2(CO)_2](PF_6)_2$, $PhCOCH_3$, and Bu_4NBr in the presence of molecular sieves 3A at -1.40 V vs. SCE.

It has been elucidated that $[Ru(bpy)_2(CO)_2]^{2+}$ is an efficient catalyst for the reduction of CO_2 in the presence of various proton sources such as H_2O,[9a)] MeOH, PhOH, and $R_nNH_{4-n}^+$ (n = 2, 3),[9b)] and that $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)(COOH)]^+$ or $[Ru(bpy)_2(CO)(COO^-)]^+$ are the precursors for the formation of CO and $HCOO^-$, respectively.[9a)] It is concluded, therefore, that $RCOCH_2R'$ plays a role of a proton source in the reactions of Eqs. 2 and 3, and the deprotonated $RCOCH_2R'$ species reacts with CO_2 to produce $RCOCHR'COO^-$ (Scheme 1). The present study has revealed that a metal complex with CO and



Scheme 1.

CO_2 ligands predominantly affords CO and $HCOO^-$ upon the electrochemical reduction of the complex. On the other hand, when CO_2 moiety ligated on a metal is utilized as a base in order to cleave a carbon-hydrogen bond of organic molecules, not only CO_2 reduction but also carboxylation of the organic molecules take place catalytically.

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10) A black precipitate appeared in the electrolysis, and about 30% of CO based on the amount of $[Ru(bpy)_2(CO)_2]^{2-}$ was confirmed in the gaseous phase.

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