Catalytic Formation of Ketones *via* Double Alkylation of Carbon Monoxide Resulting from Reductive Disproportionation of Carbon Dioxide by $[Ru(bpy)_2(qu)(CO)]^{2+}$ (bpy= 2,2'-bipyridine, qu = quinoline)

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The title complex catalyzes reductive disproportionation of CO_2 to afford CO and CO_3^{2-} in the electrochemical CO_2 reduction in the presence of $LiBF_4$, while the same reduction in the presence of $(CH_3)_4NBF_4$ in DMSO/CH_3CN produced CH_3COCH_3, $CH_3COCH_2COO^-$, and $HCOO^-$ as well as CO and CO_3^{2-}.

A number of transition metal complexes have catalytic activity for generation of CO and/or HCOOH in electro- and photochemical CO_2 reduction.[1] From the viewpoint of potential C1 sources for other organic compounds, the CO_2 reduction accompanied by carbon-carbon bond formation is much more important than two-electron reduction of CO_2. Catalytic incorporation of CO_2 to unsaturated hydrocarbons activated on metal complexes has well been documented so far. On the other hand, carbon-carbon bond formation caused by the activation of CO_2 on metal complexes has scarcely been achieved in homogeneous reactions. Recently, $HOOCCH_2OH$ and HOOCCHO were produced together with CH_3OH and HCHO in the first multi-electron reduction of CO_2 by $[Ru(bpy)(trpy)(CO)]^{2+}$ (bpy = 2,2'-bipyridine, trpy = 2,2':6'2"-terpyridine) in C_2H_5OH/H_2O at -20°C through a thermally unstable ruthenium-formyl intermediate.[2] The reduction of CO_2 activated on metal complexes in the presence of organic electrophiles in place of proton may lead to more versatile routes for catalytic carbon-carbon bond formation. This letter describes the first catalytic formation of ketones and β-keto acids via double methylation of CO resulting from reductive disproportionation of CO_2.

An ethanol solution (30 cm^3) containing $[Ru(bpy)_2Cl_2]$ (200 mg) and excess quinoline (1 ml) was refluxed for 2 h. The solution was concentrated to ca. 5 cm^3 under reduced pressure. An addition of 12% aqueous HPF_6 to the solution gave $[Ru(bpy)_2(qu)Cl](PF_6)$ as brown precipitate. A methoxyethanol solution of $[Ru(bpy)_2(qu)Cl](PF_6)$ (100 mg) and $AgPF_6$ (35 mg) was heated at 90 °C for 1 hr with vigorous CO bubbling. Precipitated AgCl powder was filtered with celite, and the filtrate was eveporated to dryness. Treatment of the product with an aqueous solution of excess NH_4PF_6 afforded $[Ru(bpy)_2(qu)(CO)](PF_6)_2$ as orange precipitate.[3] Each product was purified by column chromatography on neutral alumina using a C_6H_6/CH_3CN (1:1 v/v) eluent.

A cyclic voltammogram of $[Ru(bpy)_2(qu)(CO)](PF_6)_2$ (**1**) in CH_3CN showed three successive reversible one-electron redox waves based on the bpy and qu ligands at -1.11, -1.37, and -1.65 V (*vs*. Ag/AgCl) (a solid line in Figure 1). Introduction of CO_2 to the CH_3CN solution of **1** caused reductive current enhancement between -1.2 and -1.8 V (dotted line in Figure 1). The controlled potential electrolysis of a CO_2-saturated CH_3CN solution at -1.50 V containing **1** and Bu_4NBF_4 with a glassy carbon electrode produced $HCOO^-$ and a small amount of CO (current efficiencies of 75 and 2%, respectively). The concomitant formation of $CH_2{=}CHC_2H_5$ and Bu_3N in the electrolyte indicates that Bu_4N^+ undergoes the Hoffman elimination reaction under the present conditions and functions as a proton donor in the generation of $HCOO^-$ (eq 1).

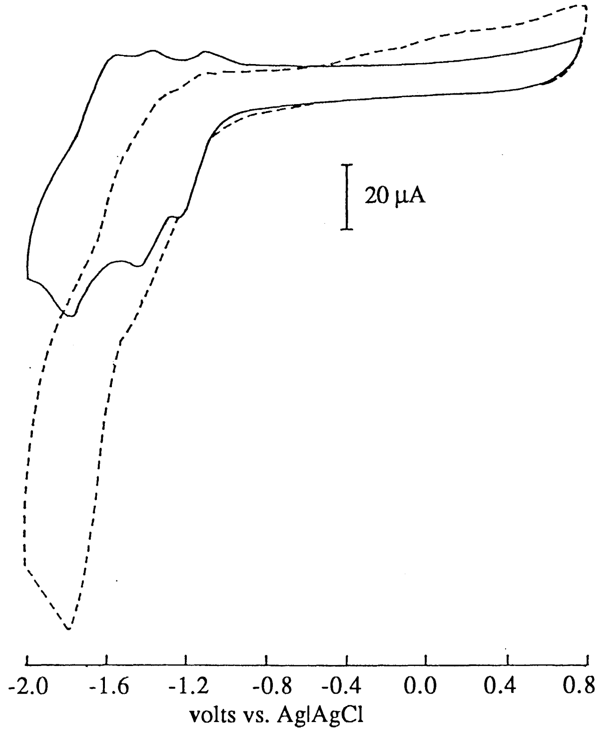

Figure 1. Cyclic voltammograms of $[Ru(bpy)_2(qu)(CO)](PF_6)_2$ in CH_3CN solution with 0.1M Bu_4NBF_4 as an electrolyte using a glassy-carbon electrode. dE/dt=100 mV/s. Solid and dotted lines are under N_2 and CO_2 atmosphere, respectively.

$$CO_2 + 2e^- + (C_4H_9)_4N^+ \longrightarrow HCOO^- + CH_2{=}CHC_2H_5 + (C_4H_9)_3N \qquad (1)$$

On the other hand, the similar electrochemical CO_2 reduction by using $LiBF_4$ as an electrolyte to avoid the participation of Bu_4N^+ in the reaction gave CO (with current efficiency, η = 78% after 10 C past) and Li_2CO_3 in CH_3CN selectively. Thus, **1** also catalyzes the reductive disproportionation of CO_2 to afford CO and CO_3^{2-} in the absence of a proton donor (eq 2).

$$2CO_2 + 2e^- \longrightarrow CO + CO_3^{2-} \qquad (2)$$

The rate of the reductive disproportionation reaction of CO_2 by **1** in the presence of $LiBF_4$ in CH_3CN (eq 2) gradually decreased due to an insulator layer of Li_2CO_3 formed on a glassy carbon electrode. On the other hand, the electrochemical CO_2 reduction by **1** in a mixed solvent of DMSO/CH_3CN (1:1 v/v) using $[(CH_3)_4N]BF_4$ under CO_2 atmosphere smoothly proceeded without deposition of $[(CH_3)_4N]_2CO_3$ on a glassy carbon electrode and unexpectedly produced $CH_3C(O)CH_3$ (η = 16.0% after 60 C past), $CH_3C(O)CH_2COO^-$ (η = 5.8%), and $HCOO^-$ (η = 6.7 %) together with CO (η = 42.0 %) and $[(CH_3)_4N]_2CO_3$. The same reductive products were also obtained in the CO_2 reduction conducted in DMSO-d_6/CH_3CN under otherwise same reaction conditions, and neither $CD_3C(O)CD_3$ nor $CD_3C(O)CH_3$ was detected by GC-MS. Furthermore, the similar electrolysis in DMSO-d_6/CH_3CN using $(C_2H_5)_4NBF_4$ in place of $(CH_3)_4NBF_4$ afforded $C_2H_5C(O)C_2H_5$ without generation of $CH_3C(O)CH_3$ and $CH_3C(O)C_2H_5$. These results indicate that CO formed in eq 2 further undergoes double methylation by $(CH_3)_4N^+$ to afford $CH_3C(O)CH_3$ (eq 3), and both $CH_3C(O)CH_2COO^-$ [4] and $HCOO^-$ are produced by subsequent carboxylation of CH_3COCH_3 by **1** under the electrolysis conditions (eq 4).

$$2CO_2 + 4e^- + 2(CH_3)_4N^+ \longrightarrow CH_3C(O)CH_3 + CO_3^{2-} + 2(CH_3)_3N \qquad (3)$$

$$CH_3C(O)CH_3 + 2e^- + 2CO_2 \longrightarrow CH_3C(O)CH_2COO^- + HCOO^- \qquad (4)$$

Indeed, those side products were predominantly generated in the electrochemical reduction of CO_2 by **1** in the presence of $CH_3C(O)CH_3$ in DMSO/CH_3CN. It is worthy to note that CO evolution was completely depressed in the electrochemical CO_2 reduction by **1** in the presence of $(CH_3)_4NBF_4$ and CH_3I (10 molar excess to **1**), and only the reactions of eqs 3 and 4 took place. In addition, $[Ru(bpy)_2(qu)(CH_3CN)]^{2+}$ was obtained after the reoxidation of the final electrolyte solution at 0.0 V.

The fact that neither CH_3CH_3 nor CH_3COO^- was formed even in the presence of CH_3I strongly indicates that $[Ru(bpy)_2(qu)(CH_3)]^+$ is not involved in the catalytic cycle of the formation of $CH_3C(O)CH_3$ (eq 3). Based on the mechanism of the electrochemical CO_2 reduction by $[Ru(bpy)(trpy)(CO)]^{2+}$ [2], the electrochemical reduction of $[Ru(bpy)_2(qu)(CH_3CN)]^{2+}$ under CO_2 also probably produces an η^1-CO_2 complex, $[Ru(bpy)_2(qu)(CO_2)]$, which reasonably explains the reductive disproportionation of CO_2 (eq 2) by the reaction with CO_2 affording CO_3^{2-} and $[Ru(bpy)_2(qu)(CO)]^{2+}$. The formation of acetone in eq 3 may, therefore, result from the double methylation of the CO ligand activated in the reduced form of the complex by $(CH_3)_4NBF_4$ or CH_3I under the electrolysis conditions. This study is the first catalytic formation of ketones and β-keto acids via double methylation of CO resulting from the reductive disproportionation of CO_2. Our continued studies are focusing on the elucidation of the whole catalytic cycle of this reaction.

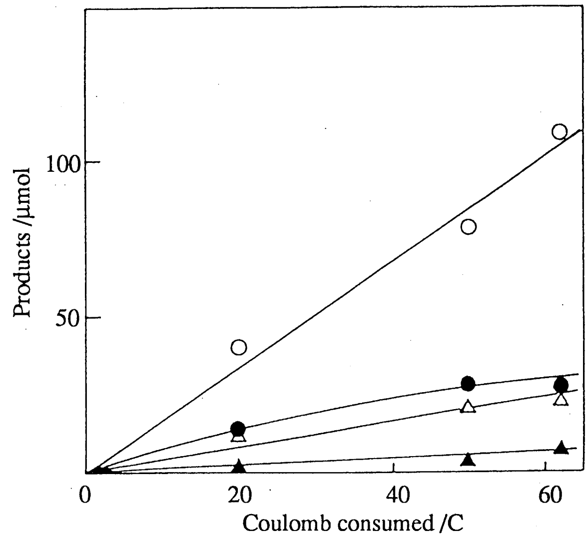

Figure 2. Plots of the amounts of CO(○), $CH_3C(O)CH_3$(●), $HCOO^-$(△), and $CH_3C(O)CH_2COO^-$ (▲) [5] against the electricity consumed in the CO_2 reduction by **1** (1.5×10^{-5} mol) in DMSO/CH_3CN (1:1 v/v)

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References and Notes

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3 Yield 58 % , Anal. Calced for $C_{30}H_{23}ON_5F_{12}P_2Ru$: C, 41.86 ; H, 2.70 ; N, 8.13. Found: C,41.82 ; H, 3.02; N, 8.32. IR(KBr): ν(C≡O) = 1992 cm^{-1}.

4 In the absence of **1**, carboxylation of $CH_3C(O)CH_3$ by $(CH_3)_3N$ and $(C_2H_5)_3N$ does not take place in CO_2-saturated CH_3CN at room temperature.

5 The amounts of CO and $CH_3C(O)CH_3$ were determined by GC, and those of $HCOO^-$ and $CH_3C(O)CH_2COO^-$ by isotachophoretic analyzer and HPLC, respectively.