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Electrochemical Reaction of CO_2 with Me_2NH to Afford N,N-Dimethylformamide, Catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2'-bipyridine)

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Electrochemical CO_2 reduction catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ in the presence of Me_2NH and $Me_2NH \cdot HCl$ in anhydrous acetonitrile catalytically produces $HCOO^-$ and N,N-dimethylformamide (DMF) with current efficiency 75.7 and 21.4%, respectively, via the carbamoyl Ru(II) complex as an intermediate, whose formation was confirmed by FT-IR and ^1H NMR spectra.

Although electrochemical CO_2 reduction catalyzed by transition metal complexes has recently been studied, the products in most cases are limited to CO and/or $HCOO^-$.1-5) The direct conversion of CO_2 to organic molecules other than $HCOO^-$, therefore, is highly desired in the viewpoint of a utilization of CO_2.6) In the course of the study on electrochemical CO_2 reductions catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2'-bipyridine), we have found that $[Ru(bpy)_2(CO)_2]^{2+}$ reacts with Me_2NH to give a carbamoyl complex $[Ru(bpy)_2(CO)C(O)NMe_2]^+$. Similar carbamoyl metal complexes have been considered as a precursor in the amide synthesis by the reaction of amine with CO, catalyzed by metal complexes under high pressures and temperatures.7) This letter reports the first electrochemical production of DMF from CO_2 and Me_2NH, catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$, via the carbamoyl complex under mild conditions.

The carbonyl group of $[Ru(bpy)_2(CO)_2]^{2+}$ undergoes a nucleophilic attack with OH^- to afford a hydroxycarbonyl complex $[Ru(bpy)_2(CO)C(O)OH]^+$.8) A similar nucleophilic attack with Me_2NH takes place in acetonitrile to give a carbamoyl complex $[Ru(bpy)_2(CO)C(O)NMe_2]^+$; the $\nu(C\equiv O)$ bands at 2050 and 2101 cm^{-1} (a broken line in Fig. 1) observed in the IR spectrum of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (13.0 mmol dm^{-3}) completely disappear upon the addition of Me_2NH (26.0 mmol dm^{-3}), and two new bands appear at 1947 and 1624 cm^{-1} (a solid line in Fig. 1). The removal of Me_2NH from the solution by bubbling N_2 or by evaporation under reduced pressure followed by dissolution in acetonitrile resulted in regeneration of the IR spectrum of $[Ru(bpy)_2(CO)_2]^{2+}$, suggesting that Me_2NH reversibly reacts with $[Ru(bpy)_2(CO)_2]^{2+}$. The 1947 and 1624 cm^{-1} bands appeared in the presence of Me_2NH may be assigned to the $\nu(C\equiv O)$ and $\nu(C=O)$, respectively, of $[Ru(bpy)_2(CO)C(O)NMe_2]^+$, since carbamoyl metal complexes was reported to exhibit the $\nu(C=O)$ bands in the 1500 - 1700 cm^{-1} range.9)

The formation of $[Ru(bpy)_2(CO)C(O)NMe_2]^+$ is supported also from the ^1H NMR spectrum of a mixture of $[Ru(bpy)_2(CO)_2]^{2+}$ (66 mmol dm^{-3}) with Me_2NH (132 mmol dm^{-3}) in acetonitrile-d_3, which shows a singlet signal at δ 2.85 (Fig. 2) as well as the methyl proton signals of $Me_2NH_2^+$ (δ 3.80) and Me_2NH (δ 2.43) at room temperature. The δ 2.85 signal may be assigned to the $N-CH_3$ proton of $[Ru(bpy)_2(CO)C(O)NMe_2]^+$, since it becomes broaden with decreasing the temperature and splits into two signals with the same intensity below -30 °C (Fig. 2) owing to the restriction of free rotation around the N-C bond. Several attempts to isolate $[Ru(bpy)_2(CO)C(O)NMe_2]^+$ have been unsuccessful to recover the starting complex $[Ru(bpy)_2(CO)_2](PF_6)_2$. This may be due to the fact that $[Ru(bpy)_2(CO)C(O)NMe_2]^+$ exists as an equilibrium mixture with $[Ru(bpy)_2(CO)_2]^{2+}$ in acetonitrile in the presence of Me_2NH,[10] as expressed by Eq. 1.[11]

$$[Ru(bpy)_2(CO)_2]^{2+} + 2Me_2NH \rightleftharpoons [Ru(bpy)_2(CO)C(O)NMe_2]^+ + Me_2NH_2^+ \quad (1)$$

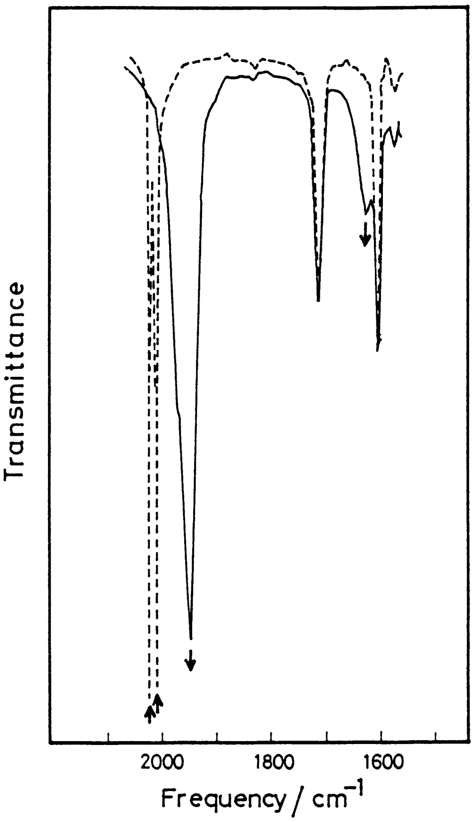


Fig. 1. FT-IR spectra of $[Ru(bpy)_2(CO)_2]^{2+}$ in acetonitrile in the presence (——) and absence (---) of Me_2NH.

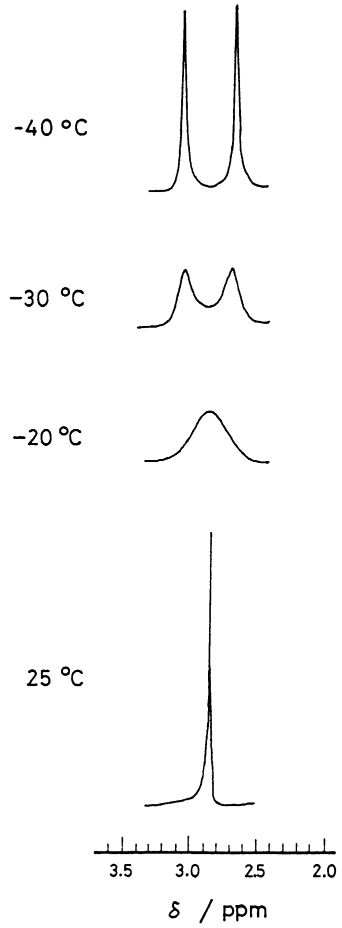


Fig. 2. Temperature dependence of the methyl proton signals of $[Ru(bpy)_2(CO)C(O)NMe_2]^+$ in CD_3CN.

The controlled potential electrolysis was performed on an Hg working electrode at -1.30 V vs. SCE for a CO_2-saturated acetonitrile solution (15 cm^3)

containing $[Ru(bpy)_2(CO)_2]^{2+}$ (5.7 mg, 7.5 μmol), $Bu^n{}_4NClO_4$ (0.51 g, 1.5 mmol), Me_2NH (7.5 mmol), $Me_2NH{\cdot}HCl$ (0.25 g, 3.0 mmol) and Na_2SO_4 as dehydration chemicals (ca. 3 g). As the result, two-electron reductions take place to produce not only $HCOO^-$, CO, and H_2 but also DMF (Eqs. 2 - 5). The amounts of these products[12] increase linearly with the electricity consumed in the reduction, and the turnover number for the formation of DMF is more than 10 (based on the amount of $[Ru(bpy)_2(CO)_2]^{2+}$) at the consumption of 75 C, as depicted in Fig. 3. The current efficiency for the formation of $HCOO^-$, CO, H_2, and DMF were 75.7, 1.0, 0.7, and 21.4%,[13] respectively, suggesting that any reactions other than Eqs. 2 - 5 hardly take place. Recently, the authors have reported that the active species for the formation of $HCOO^-$ in the electrochemical CO_2 reduction catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ is $[Ru(bpy)_2(CO)C(O)OH]^+$ (or $[Ru(bpy)_2(CO)(COO^-)]^+$), which is stable in alkaline media, while the active species for the formation of CO is $[Ru(bpy)_2(CO)_2]^{2+}$ being stable in acidic media.[1] A high current efficiency for the formation of $HCOO^-$ in the present study may, therefore, result from a large pK_a value of $Me_2NH_2{}^+$ (15.8 in acetonitrile) used as a proton source.[2]

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

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O \qquad (3)$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (4)$$

$$CO_2 + Me_2NH + 2H^+ + 2e^- \longrightarrow \mathrm{H}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NMe_2} + H_2O \qquad (5)$$

Scheme 1 shows a possible catalytic cycle for the present reaction. As reported previously,[1] $[Ru(bpy)_2(CO)_2]^{2+}$ undergoes a simultaneous two-electron reduction to give $[Ru(bpy)_2(CO)]^0$ with liberating a CO molecule in the absence of Me_2NH.[1] The penta-coordinated Ru(0) complex reacts with CO_2 to yield $[Ru(bpy)_2(CO)(COO^-)]^+$, which exists as an equilibrium mixture with $[Ru(bpy)_2(CO)C(O)OH]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$; the amount of each species depends on the proton concentration in the reaction mixture,

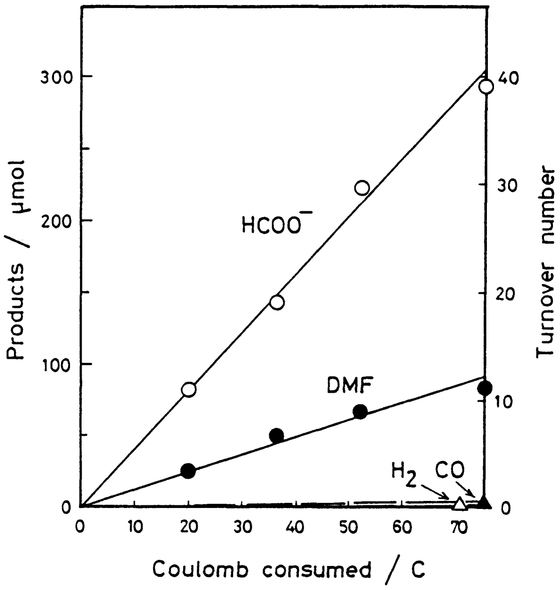
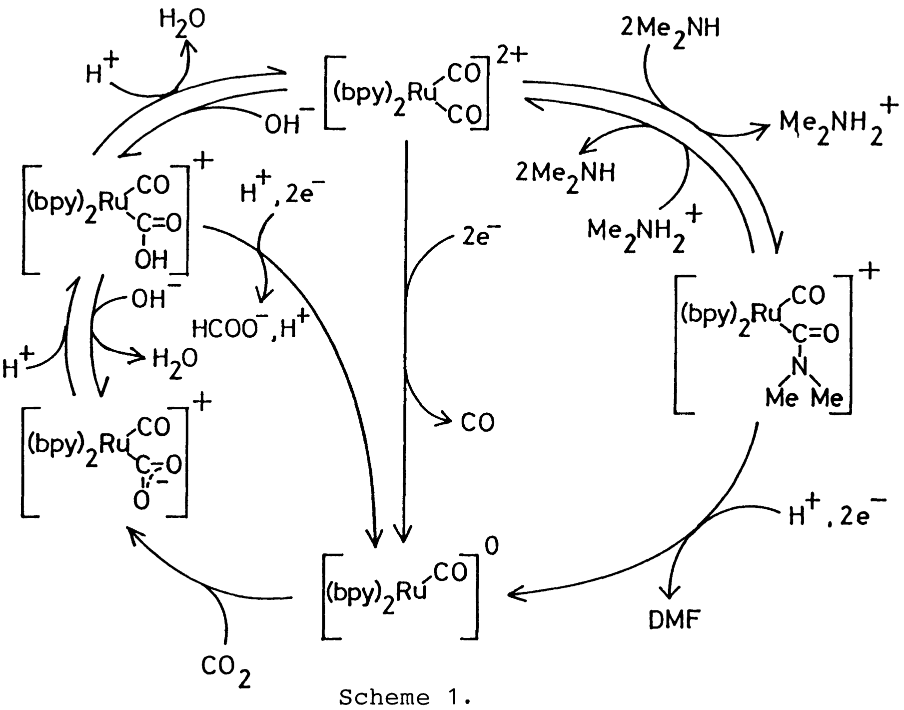


Fig. 3. Amounts of the products in the electrolysis (-1.30 V vs. SCE) of a CO_2-saturated acetonitrile solution containing $[Ru(bpy)_2(CO)_2](PF_6)_2$, $Bu^n{}_4NClO_4$, Me_2NH, $Me_2NH{\cdot}HCl$ and Na_2SO_4 at 30 °C.

and the latter two are reduced with two electrons to produce $HCOO^-$ and CO, respectively. In the presence of Me_2NH, $[Ru(bpy)_2(CO)_2]^{2+}$ effectively reacts with the amine to produce $[Ru(bpy)_2(CO)C(O)NMe_2]^+$, which undergoes two-electron reduction to afford DMF[14] with regenerating the penta-coordinated Ru(0) species $[Ru(bpy)_2(CO)]^0$, which is subject to addition of CO_2, as described above.



Scheme 1.

References
1) H. Ishida, K. Tanaka, and T. Tanaka, Chem. Lett., 1985, 405; Organometallics, 6, 181 (1987).
2) H. Ishida, H. Tanaka, K. Tanaka, and T. Tanaka, J. Chem. Soc., Chem. Commun. in press.
3) B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining, and T. J. Meyer, J. Chem. Soc., Chem. Commun., 1985, 1414.
4) S. Slater and J. H. Wagenknecht, J. Am. Chem. Soc., 106, 5367 (1984).
5) M. Beley, J. P. Collin, R. Ruppert, and J. P. Sauvage, J. Chem. Soc., Chem. Commun., 1984, 1315; J. Am. Chem. Soc., 108, 7461 (1986).
6) S. Torii, H. Tanaka, T. Hamatani, K. Morisaki, A. Jutand, F. Peluger, and J. F. Fauvarque, Chem. Lett., 1986, 169.
7) H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, J. Am. Chem. Soc., 75, 3148 (1953).
8) K. Tanaka, M. Morimoto, and T. Tanaka, Chem. Lett., 1983, 901; H. Ishida, K. Tanaka, and T. Tanaka, Organometallics, 5, 724, (1986).
9) W. Jetz and R. J. Angelici, J. Am. Chem. Soc., 94, 3799 (1972).
10) R. J. Angelici, Acc. Chem. Res., 5, 335 (1972); R. J. Angelici and L. J. Blacik, Inorg. Chem., 11, 1754 (1972).
11) The equilibrium constant for Eq. 1 was determined as 1.67×10^7 mol^{-2} dm^6 at 25 °C by the change of electronic absorption spectra of $[Ru(bpy)_2(CO)_2]^{2+}$ in the presence of various amounts of Me_2NH in acetonitrile.
12) CO, H_2, and DMF were determined by the gaschromatography, and $HCOO^-$ by an isotachophoretic analyzer.
13) In the absence of Na_2SO_4, the current efficiency for the formation of DMF was gradually decreased with the progress of the reduction, since the adduct formation between Me_2NH and $[Ru(bpy)_2(CO)_2]^{2+}$ is strongly hindered by H_2O formed in the reation of Eqs. 2 and 5.
14) No DMF was formed in the reaction of Me_2NH with either HCOOH or CO in the presence of $[Ru(bpy)_2(CO)_2]^{2+}$ at 30 °C.

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