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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, <u>via</u> 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 Me₂NH to give a carbamoyl complex $[Ru(bpy)_2(CO)C(0)NMe_2]^+$. 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 Me₂NH, catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$, <u>via</u> 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 $[Ru(bpy)_2(CO)C(0)OH]^{+,8}$ A similar nucleophilic attack with Me₂NH takes place in acetonitrile to give a carbamoyl complex $[Ru(bpy)_2(CO)C(0)NMe_2]^+$; the $v(C\equiv 0)$ 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 Me₂NH (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 Me₂NH from the solution by bubbling N₂ 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 Me₂NH reversibly reacts with $[Ru(bpy)_2(CO)_2]^{2+}$. The 1947 and 1624 cm⁻¹ bands appeared in the presence of Me₂NH may be assigned to the v(C=0) and v(C=0), respectively, of $[Ru(bpy)_2(CO)C(0)NMe_2]^+$, since carbamoyl metal complexes was reported to exhibit the v(C=0) 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 Me₂NH (132 mmol dm⁻³) in acetonitrile-d₃, which shows a singlet signal at δ 2.85 (Fig. 2) as well as the methyl proton signals of Me₂NH₂⁺ (δ 3.80) and Me₂NH (δ 2.43) at room temperature. The δ 2.85 signal may be assigned to the N-CH₃ 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 Me₂NH,¹⁰) as expressed by Eq. 1.¹¹







The controlled potential electrolysis was performed on an Hg working electrode at -1.30 V <u>vs</u>. SCE for a CO_2 -saturated acetonitrile solution (15 cm³)

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 (<u>ca.</u> 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 products¹²⁾ 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, H₂, 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 CO₂ reduction catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ is $[Ru(bpy)_2(CO)(CO)H]^+$ (or $[Ru(bpy)_2(CO)(CO)^-]^+$),

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 Me₂NH₂⁺ (15.8 in acetonitrile) used as a proton source.²)

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 Me₂NH.¹⁾ The penta-coordinated Ru(0) complex reacts with CO₂ 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 <u>vs.</u> 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, In the presence of Me_2NH , $[Ru(bpy)_2(CO)_2]^{2+}$ effectively reacts respectively. 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.



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 11) The equilibrium constant for Eq. 1 was determined as 1.67 x 10⁷ mol⁻² dm⁶ at 25 °C by the change of electronic absorption spectra of [Ru(bpy)₂(CO)₂]²⁺ in the presence of various amounts of Me₂NH in acetonitrile.
 12) CO, H₂, and DMF were determined by the gaschromatography, and HCOO⁻ by an isotachophoretic analyzer.
- 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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