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Osaka University

# STUDIES ON CARBON DIOXIDE FIXATION CATALYZED BY RUTHENIUM COMPLEXES

(ルテニウム錯体触媒による二酸化炭素)  
固定反応に関する研究

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## Preface

The work of this thesis were mainly carried out under the guidance of Professor Toshio Tanaka at Department of Applied Chemistry, Faculty of Engineering, Osaka University; a part of the work at Department of Applied Chemistry, Faculty of Engineering, Kumamoto University.

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## List of Publications

- (1) "The Electrochemical Reduction of CO<sub>2</sub> Catalyzed by Ruthenium Carbonyl Complexes"  
Hitoshi Ishida, Koji Tanaka, and Toshio Tanaka  
Chemistry Letters, 1985, 405.
- (2) "Isolation of Intermediates in the Water Gas Shift Reactions Catalyzed by [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup> and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>"  
Hitoshi Ishida, Koji Tanaka, Masaru Morimoto, and Toshio Tanaka  
Organometallics, 1986, 5, 724.
- (3) "Electrochemical CO<sub>2</sub> Reduction Catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup>. The Effect of pH on the Formation of CO and HCOO<sup>-</sup>"  
Hitoshi Ishida, Koji Tanaka, and Toshio Tanaka  
Organometallics, 1987, 6, 181.
- (4) "Selective Formation of HCOO<sup>-</sup> in the Electrochemical CO<sub>2</sub> Reduction Catalysed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> (bpy = 2,2'-bipyridine)"  
Hitoshi Ishida, Hiroaki Tanaka, Koji Tanaka, and Toshio Tanaka  
J. Chem. Soc., Chem. Commun., 1987, 131.
- (5) "Electrochemical Reaction of CO<sub>2</sub> with Me<sub>2</sub>NH to Afford N,N-Dimethylformamide, Catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> (bpy = 2,2'-

- bipyridine)"
- Hitoshi Ishida, Hiroaki Tanaka, Koji Tanaka, and Toshio Tanaka  
Chemistry Letters, 1987, 597.
- (6) "Photoreduction of CO<sub>2</sub> in the [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> / [Ru(bpy)<sub>3</sub>]<sup>2+</sup>  
or [Ru(phen)<sub>3</sub>]<sup>2+</sup> / Triethanolamine / N,N-Dimethylformamide  
System"
- Hitoshi Ishida, Koji Tanaka, and Toshio Tanaka  
Chemistry Letters, 1987, 1035.
- (7) "Photochemical CO<sub>2</sub> Reduction by an NADH Model Compound in the  
presence of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> (bpy = 2,2'-  
bipyridine) in H<sub>2</sub>O / DMF"
- Hitoshi Ishida, Koji Tanaka, and Toshio Tanaka  
Chemistry Letters, 1988, 339.
- (8) "Photochemical CO<sub>2</sub> Reduction Catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>  
Using Triethanolamine and 1-Benzyl-1,4-dihydronicotinamide  
as an Electron Donor"
- Hitoshi Ishida, Tohru Terada, Koji Tanaka, and Toshio  
Tanaka  
Inorg. Chem. in press.
- (9) "Ligand Effects of the Ruthenium 2,2'-Bipyridine and 1,10-  
Phenanthroline Complexes on Electrochemical CO<sub>2</sub> Reductions"
- Hitoshi Ishida, Katsuyuki Fujiki, Koji Tanaka, Tohru Terada,

Toshio Tanaka, and Katsutoshi Ohkubo

J. Chem. Soc., Dalton Trans. in contribution.

- (10) "N,N-dimethylformamide Generation from Electrochemical CO<sub>2</sub> Reduction Catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>"

Hitoshi Ishida, Tomoyuki Ohba, Katsuyuki Fujiki, Hiroaki Tanaka, Koji Tanaka, Toshio Tanaka, and Katsutoshi Ohkubo in preparation.

#### List of Supplementary Papers

- (1) "Highly Efficient Enantioselective Hydrolysis of Short Chain N-Acetyl Amino Acid p-Nitrophenyl Esters Catalysed by Esterase Models"

Katsutoshi Ohkubo, Masahiko Kawata, Takashi Orito, and Hitoshi Ishida

J. Chem. Soc., Perkin Trans. 1, **1989**, 666.

- (2) "Stereoselective Dioxygenation of a Racemic Tryptophan Derivative Catalysed by Chiral Manganese Porphyrins"

Katsutoshi Ohkubo, Takashi Sagawa, Mutsuo Kuwata, Tsuguru Hata, and Hitoshi Ishida

J. Chem. Soc., Chem. Commun., **1989**, 352.

- (3) "Stereoselective Dioxygenation of a Tryptophan Derivative

Catalyzed by a Manganese Porphyrin Included in Bovine Serum Albumin"

Katsutoshi Ohkubo, Hitoshi Ishida, and Takashi Sagawa  
J. Mol. Cat., 1989, 53, L5.

- (4) "Photoinduced Enantioselective and Catalytic Reduction of  $\text{Co}(\text{acac})_3$  with a Chiral Ruthenium Photosensitizer"

Katsutoshi Ohkubo, Taisuke Hamada, Tohru Inaoka, and Hitoshi Ishida, Inorg. Chem., 1989, 28, 2021.

- (5) "Micellar Effects on Reduction of Tris(acetylacetonato)-cobalt(III) by 1-Benzyl-1,4-dihydronicotinamide with Ionic Surfactants"

Kohichi Yamashita, Hitoshi Ishida, and Katsutoshi Ohkubo  
J. Chem. Soc., Perkin Trans. 2 in press.

- (6) "Enantioselective Electron Transfer Reaction Catalyzed by a Novel Photosensitizer,  $[\text{Ru}(\text{S}(-) \text{ or } \text{R}(+) \text{-PhEt}^* \text{bpy})_3]^{2+}$ "

Katsutoshi Ohkubo, Hitoshi Ishida, Taisuke Hamada, and Tohru Inaoka  
Chemistry Letters, 1989, 1545.

## Contents

General Introduction	1
Chapter 1 Water Gas Shift Reaction Catalyzed by Ruthenium Complexes; Mechanism and Isolation of the Reaction Intermediates	3
Chapter 2 Electrochemical CO <sub>2</sub> Reduction Catalyzed by Ruthenium Complexes; the Effect of pH on the Formation of CO and HCOO <sup>-</sup>	34
Chapter 3 Selective HCOO <sup>-</sup> Formation on the Electrochemical CO <sub>2</sub> Reduction	64
Chapter 4 Ligand Effect of the Ruthenium Complexes on Electrochemical CO <sub>2</sub> Reduction	75
Chapter 5 Generation of N,N-Dimethylformamide by the Electrochemical CO <sub>2</sub> Reduction with (CH <sub>3</sub> ) <sub>2</sub> NH, Catalyzed by a Ruthenium Complex	97
Chapter 6 Photochemical and Catalytic Reduction of CO <sub>2</sub> in the [Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup> / [Ru(bpy) <sub>3</sub> ] <sup>2+</sup> / Triethanolamine / N,N-Dimethylformamide System	110



Chapter 7	Photochemical CO <sub>2</sub> Reduction with an NADH Model Compound, Catalyzed by Ruthenium Complexes	129
Conclusion		142
Acknowledgments		146

## General Introduction

Almost all the organic compounds on the earth are derived from substances produced by photosynthesis, in which the  $\text{CO}_2$  fixation is performed by using electrons obtained from  $\text{H}_2\text{O}$ . Chemists have long dreamed of imitating this reaction in a test tube, because the artificial photosynthesis is expected to solve the problem of shortage of fuel, resources and energy. Especially, the increase of carbon dioxide concentrations in air becomes one of the recent social problems.

Although a number of organic synthesis with carbon dioxide as a starting material have been developed, carbon dioxide has been employed only for industrial use of urea synthesis, and on a small scale, of the Kolbe-Schmitt reaction until now. In laboratories, the reaction between Grignard reagents and carbon dioxide is practically important in the synthesis of carboxylic acid. In the development of organotransition metal chemistry, there have been numerous papers which report the reactions of a transition metal alkyls and hydrides with carbon dioxide to give the corresponding carboxylic acids and formic acid, respectively. However, catalytic fixation of carbon dioxide by transition metal complexes has scarcely been reported.

The objects of this thesis are to search the efficient catalysts for  $\text{CO}_2$  reduction, and to clarify catalytic properties and mechanisms of the reaction. Other objects are to convert carbon dioxide to more useful organic molecules, and to develop

photochemical CO<sub>2</sub> reductions as artificial photosyntheses.

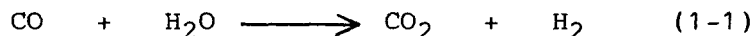
Chapter 1 describes the Water Gas Shift (WGS) reaction catalyzed by ruthenium complexes as the reverse reaction of CO<sub>2</sub> reduction, especially, the isolation and properties of reaction intermediates. It is described in chapter 2 that [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup>, which are catalysts for the WGS reactions, catalyze electrochemical CO<sub>2</sub> reductions to afford CO and HCOO<sup>-</sup> in aqueous DMF solutions with low and high pH, respectively. In chapter 3, selective HCOO<sup>-</sup> formation in the electrochemical CO<sub>2</sub> reductions with organic acids having low pK<sub>a</sub> values in anhydrous acetonitrile is discussed. Chapter 4 describes ligand effects of the ruthenium catalysts on the electrochemical CO<sub>2</sub> reduction in connection with the reduction potentials and the equilibrium reactions with OH<sup>-</sup>. Chapter 5 describes electrochemical preparation of N,N-dimethylformamide from CO<sub>2</sub> and dimethylamine, catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>. It is discussed in chapter 6 that photochemical CO<sub>2</sub> reduction has been performed by irradiation of visible light to the CO<sub>2</sub>-saturated N,N-dimethylformamide / triethanolamine solutions containing [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>, giving selective HCOO<sup>-</sup> formation. Chapter 7 describes photochemical CO<sub>2</sub> reduction with 1-benzyl-1,4-dihydronicotinamide, a model compound of NADH, which acts as electron donor in the photosynthetic systems.

## CHAPTER 1

### Water Gas Shift Reaction Catalyzed by Ruthenium Complexes; Mechanism and Isolation of the Reaction Intermediates

#### 1-1 Introduction

The water gas shift (WGS) reaction, in which carbon monoxide is oxidized by water to give carbon dioxide and dihydrogen (eq. 1-1), is the reverse reaction of CO<sub>2</sub> reduction. One possibility



of catalytic CO<sub>2</sub> reduction is to cause the reverse reaction of WGS reaction by using transition metal catalysts. Therefore, the study on catalysts for the WGS reaction is important also for the CO<sub>2</sub> reduction.

Since the homogeneous WGS reaction catalyzed by transition metal complexes was reported in 1977<sup>1</sup>, a number of homogeneous WGS reactions under mild conditions have been studied by employing mono- and polynuclear transition metal carbonyl complexes,<sup>2,3</sup> of which ruthenium carbonyl clusters have attracted much attention as active catalysts for the WGS reaction.<sup>4</sup> The WGS reaction catalyzed by transition metal complexes in alkaline media at elevated temperatures has been suggested to involve the

following key steps: (i) a nucleophilic attack of  $\text{OH}^-$  or  $\text{H}_2\text{O}$  on the carbon atom of CO coordinated to transition metals, giving a hydroxycarbonyl complex (eq. 1-2),<sup>5, 6</sup> (ii) thermal decarboxylation of the hydroxycarbonyl complex to afford  $\text{CO}_2$  and a metal hydride (eq. 1-3), and (iii)  $\text{H}_2$  evolution by the reaction



of the metal hydride with protons or water. However, few hydroxycarbonyl, hydride, and aquo intermediates involved in each step have been confirmed mechanistically so far. This chapter describes the WGS reaction catalyzed by  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  (bpy = 2,2'-bipyridine) which is a catalyst precursor in aqueous alkaline solutions, as well as mechanisms of the reaction, based on systematic isolation of all the possible intermediates.

## 1-2 Experimental Section

**Materials.** Bis(2,2'-bipyridine)dichlororuthenium(II),  $\text{Ru}(\text{bpy})_2\text{Cl}_2$ ,<sup>7</sup> tris(2,2'-bipyridine)ruthenium(II) dichloride,  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ,<sup>8</sup> and bis(2,2'-bipyridine)carbonylhydrido-ruthenium(II) hexafluorophosphate,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$ <sup>9</sup> were prepared according to the literatures. A  $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$  (1:1 v/v, 50  $\text{cm}^3$ ) solution containing both  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (420 mg, 0.81

mmol) and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (200 mg, 0.82 mmol) was stirred in a sealed tube at  $120^\circ\text{C}$  for 18 h. The solution was cooled to room temperature to give a black precipitate of  $(\text{bpy})_2\text{Ru}-\text{O}-\text{Mo}-\text{O}(\text{O})_2$ , which was collected by filtration, washed with water, ethanol, and then diethyl ether, and dried in vacuo, 51% yield; mp  $150^\circ\text{C}$  (dec.). Anal. Calcd for  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{MoO}_4\text{Ru}$ : C, 41.90; H, 2.81; N, 9.77%. Found: C, 41.42; H, 2.89; N, 9.83%.

**Preparation of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ .** An ethylene glycol solution ( $100 \text{ cm}^3$ ) containing  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (137 mg, 0.26 mmol) and a catalytic amount of  $\text{Ru}(\text{bpy})_2\text{O}_2\text{MoO}_2$  (12 mg, 0.02 mmol) was refluxed for 6 h, during which time the color of the solution changed from purple to reddish brown. After cooled to room temperature, the solution was evaporated to about a quarter volume in vacuo, followed by the addition of water ( $50 \text{ cm}^3$ ). The resulting solution was filtered, and the filtrate was mixed with an aqueous ( $5 \text{ cm}^3$ ) solution of  $\text{NH}_4\text{PF}_6$  (200 mg, 1.2 mmol) to afford an orange precipitate, which was filtered and the filtrate was chromatographed on alkaline alumina using  $\text{CH}_3\text{CN}/\text{C}_6\text{H}_6$  (1:1 v/v) as an eluent, and then recrystallized from  $\text{CH}_3\text{CN}/\text{C}_6\text{H}_6$ , 80% yield; mp.  $290^\circ\text{C}$  (dec.),  $\nu(\text{C}\equiv\text{O}) 1960 \text{ cm}^{-1}$ . Anal. Calcd for  $\text{C}_{21}\text{H}_{16}\text{ClF}_6\text{N}_4\text{OPRu}$ : C, 40.56; H, 2.59; N, 9.01%. Found: C, 40.27; H, 2.64; N, 9.16%.

**Preparation of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$ .** An aqueous ( $15 \text{ cm}^3$ ) suspension of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$  (354 mg, 0.57 mmol) under 10

kg/cm<sup>2</sup> of CO in a stainless-steel bomb was stirred magnetically at 150°C for 20 h. After the bomb was cooled to room temperature, the CO pressure was released. The resulting colorless solution was filtered. To the filtrate was added NH<sub>4</sub>PF<sub>6</sub> (810 mg, 5.0 mmol) dissolved in a small amount of water (5 cm<sup>3</sup>) to yield a white precipitate, which was collected by filtration and crystallized from CH<sub>3</sub>CN/C<sub>6</sub>H<sub>6</sub> (1:1 v/v), 70% yield; mp. 280°C,  $\nu(\text{C}\equiv\text{O})$  2040, 2085 cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>16</sub>F<sub>12</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Ru: C, 34.80; H, 2.12; N, 7.38%. Found: C, 34.98; H, 2.29; N, 7.65%.

**Preparation of [Ru(bpy)<sub>2</sub>(CO)(H<sub>2</sub>O)][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O.** An aqueous acidic solution (400 cm<sup>3</sup>) of [Ru(bpy)<sub>2</sub>(CO)H](PF<sub>6</sub>) (50 mg, 0.085 mmol) at pH 4.0 (adjusted with 1.0 N HCl) was stirred for 1 h at room temperature and then concentrated to about a half volume under reduced pressures. To the resulting solution was added NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> (120 mg, 0.35 mmol) dissolved in a small amount of water (5 cm<sup>3</sup>) at pH 4.0 to afford a yellow precipitate, which was collected by filtration and recrystallized from CH<sub>3</sub>OH/H<sub>2</sub>O (pH 4.0), 50% yield; mp. 120°C (dec.), the amount of H<sub>2</sub>O solvated was determined by <sup>1</sup>H nmr in CD<sub>3</sub>CN,  $\nu(\text{C}\equiv\text{O})$  1990 cm<sup>-1</sup>,  $\nu(\text{O}-\text{H})$  3040 cm<sup>-1</sup>. Anal. Calcd for C<sub>69</sub>H<sub>60</sub>B<sub>2</sub>N<sub>4</sub>O<sub>3</sub>Ru: C, 73.05; H, 5.51; N, 4.94%. Found: C, 72.76; H, 5.34; N, 5.30%.

**Preparation of [Ru(bpy)<sub>2</sub>(CO)(OH)](PF<sub>6</sub>)·H<sub>2</sub>O.** An aqueous acidic solution (100 cm<sup>3</sup>) of [Ru(bpy)<sub>2</sub>(CO)H](PF<sub>6</sub>) (51 mg, 0.087 mmol) at pH 4.0 (adjusted with 1.0 N HCl) was stirred for 1 h at

room temperature, and 1.0 N NaOH was then added to adjust the pH of the solution to 9.5. The resulting solution was filtered, and the filtrate was concentrated to about a quarter volume under reduced pressures, followed by adjusting the pH value to 11 to produce an orange precipitate, which was collected by filtration and dried in vacuo, 30% yield; mp. 200°C (dec.), the amount of H<sub>2</sub>O solvated was determined by <sup>1</sup>H nmr in CD<sub>3</sub>CN,  $\nu(\text{C}\equiv\text{O})$  1980 cm<sup>-1</sup>,  $\nu(\text{O-H})$  3050 cm<sup>-1</sup>. Anal. Calcd for C<sub>21</sub>H<sub>19</sub>F<sub>6</sub>N<sub>4</sub>O<sub>3</sub>PRu: C, 40.59; H, 3.08; N, 9.01%. Found: C, 40.32; H, 2.84; N, 8.87%.

**Preparation of [Ru(bpy)<sub>2</sub>(CO)C(O)OH](PF<sub>6</sub>)<sub>2</sub>·1/2H<sub>2</sub>O.** An aqueous solution (300 cm<sup>3</sup>) of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (144 mg, 0.19 mmol) at pH 9.5 (adjusted with 0.2 N NaOH) was concentrated to ca. 20 cm<sup>3</sup> under reduced pressures, and the pH value was adjusted to 10 to produce a yellow precipitate, which was collected by filtration, washed with ether, and dried in vacuo, 20% yield; mp. 155°C (dec.), the amount of H<sub>2</sub>O solvated was determined by <sup>1</sup>H nmr in CD<sub>3</sub>CN,  $\nu(\text{O-H})$  3070 cm<sup>-3</sup>,  $\nu(\text{C}\equiv\text{O})$  1960 cm<sup>-1</sup>,  $\nu(\text{C=O})$  1587 cm<sup>-1</sup>,  $\nu(\text{C-O})$  1140 cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>F<sub>6</sub>N<sub>4</sub>O<sub>3.5</sub>PRu: C, 41.26; H, 2.83; N, 8.75%. Found: C, 41.08; H, 2.82; N, 8.87%.

**Preparation of [Ru(bpy)<sub>2</sub>(CO)C(O)OCH<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>·1/2CH<sub>2</sub>Cl<sub>2</sub>.** An anhydrous CH<sub>3</sub>OH (50 cm<sup>3</sup>) solution containing [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (77 mg, 0.10 mmol) and CH<sub>3</sub>ONa (0.29 mmol) was stirred for 1 h under N<sub>2</sub> atmosphere at room temperature. The resulting solution was evaporated to dryness under reduced pressures. The



crude product thus obtained was dissolved in  $\text{CH}_2\text{Cl}_2$  ( $90 \text{ cm}^3$ ), and the solution was dried with  $\text{Na}_2\text{SO}_4$ . The resulting solution was filtered, and the filtrate was evaporated to ca.  $5 \text{ cm}^3$ , giving a yellow solid, 80% yield; mp.  $110^\circ\text{C}$  (dec.), the amount of  $\text{CH}_2\text{Cl}_2$  solvated was determined by  $^1\text{H}$  nmr in  $\text{CD}_3\text{CN}$ ,  $\nu(\text{C}\equiv\text{O})$   $1960 \text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{O})$   $1605 \text{ cm}^{-1}$ ,  $\nu(\text{C}-\text{O})$   $1045 \text{ cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23.5}\text{H}_{20}\text{Cl}-\text{F}_6\text{N}_4\text{O}_3\text{PRu}$ : C, 41.03; H, 2.93; N, 8.14%. Found: C, 41.02; H, 3.28; N, 7.86%.

**General Procedure for the WGS Reaction Studies.** The WGS reaction was carried out in a stainless-steel bomb ( $65 \text{ cm}^3$ ) containing a glass tube in which a ruthenium catalyst (0.05 mmol) and an aqueous KOH solution ( $0.21 \text{ mol dm}^{-3}$ ,  $15 \text{ cm}^3$ ) were placed. After degassed by three  $10 \text{ kg/cm}^2$  pressurization/depressurization cycles with CO, the bomb was pressurized with  $3\text{-}20 \text{ kg/cm}^2$  of CO and kept at the reaction temperature for 20 h with stirring magnetically. After the bomb was cooled to room temperature, gaseous products in the vapor phase were sampled with a gas syringe through a septum cap attached to the exit of the tap and analyzed with a Shimadzu GC-7A gas chromatograph equipped with TCD using a 60/80 mesh Unibeads 1S under  $\text{N}_2$  carrier gas. A Shimadzu Chromatopack C-E1B digital integrator was used to integrate the output from the gas chromatograph.

**Physical Measurements.** Electronic and infrared spectra were measured with Union SM-401 and Hitachi 215 spectrophotome-

ters, respectively.  $^1\text{H}$  nmr spectra were recorded on a JEOL PS-100 spectrometer. pH Values of the reaction mixture were determined with a Toa Denpa Model GS-135 pH electrode. Equilibrium constants were determined by electrophotometry or potentiometric titration at  $25^\circ\text{C}$ . The kinetic measurement for the nucleophilic attack of  $\text{OH}^-$  to  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  was carried out in  $\text{H}_2\text{O}$  under the pseudo-first-order conditions with at least 5-fold excess amounts of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  ( $2.63 \times 10^{-4} \text{ mol dm}^{-3}$ ) in an aqueous KOH solution. The rate of reaction was measured by monitoring the absorbance at 440 nm due to  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  in the reaction mixture, using a Union RA-413 stopped-flow spectrophotometer equipped with a 2 mm length quartz cell in a cell holder thermostated within  $25.0 \pm 0.2^\circ\text{C}$ . Pseudo-first-order rate constants were obtained from the slope of plots of  $\log|A_t - A_\infty|$  against time, which was found to be linear for at least 3 half-lives, where  $A_t$  and  $A_\infty$  are absorbances at a time  $t$  and the end of the reaction, respectively.

### 1-3 Results and Discussion

**Catalytic Reactions and the Isolation of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$ .** It has already been reported that  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]\text{Cl}$  and  $[\text{Ru}(\text{phen})_2(\text{CO})\text{Cl}]\text{Cl}$  (phen = 1,10-phenanthroline) catalyze the photochemical WGS reaction in aqueous solutions under mild conditions (1 - 3  $\text{kg/cm}^2$  of CO,  $100 - 160^\circ\text{C}$ ).<sup>10</sup> We have found, however, that  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$  is still active for the WGS

reaction without irradiation in aqueous alkaline solutions, as shown in Table 1-I. Although the turnover number for the H<sub>2</sub> formation in the present study using [Ru(bpy)<sub>2</sub>(CO)Cl](PF<sub>6</sub>) as a catalyst in the presence of KOH (3.2 mmol) was only 3.8 for 20 h under a pressure of 3 kg/cm<sup>2</sup> of CO at 100°C (entry 1, Table 1-I), it increases with increasing the reaction temperature and the CO pressure (compare entry 1 with 2, entries 3 and 4 with 5, and entry 2 with 4, Table 1-I). The maximum turnover number in the present study was 502 under 20 kg/cm<sup>2</sup> of CO at 150°C (entry 5, Table 1-I), while the theoretical one expected from the volume of the bomb used in this study is 800 under the initial pressure of 20 kg/cm<sup>2</sup> of CO. No further attempt to increase the turnover number has been performed, since the purposes of this work are to explore the active species in the WGS reaction and to clarify the mechanisms.<sup>11</sup>

The discrepancy in the amounts of H<sub>2</sub> and CO<sub>2</sub> evolved in the gas phase (Table 1-I) may result from the higher solubility of CO<sub>2</sub> than H<sub>2</sub> in addition to the formation of the carbonate ion in alkaline solutions as suggested previously.<sup>12</sup> In fact, the amount of CO<sub>2</sub> dissolved in the final solutions obtained after releasing the pressures in the bomb was determined as 20 - 30 wt% of that in the gas phase by gas chromatography. The [Ru(bpy)<sub>2</sub>(CO)Cl](PF<sub>6</sub>) complex was gradually decomposed in the course of the WGS reaction for 20 h, finally giving a solution of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, as confirmed from the electronic absorption spectrum, with a pale green precipitate. The catalytic activity of [Ru-

**Table 1-I.** The Water Gas Shift Reaction

Entry	Catalyst <sup>a</sup>	Temp °C	CO kg cm <sup>-2</sup>	KOH <sup>b</sup> mmol	Gaseous product <sup>c</sup>	
					H <sub>2</sub>	CO <sub>2</sub>
1	[Ru(bpy) <sub>2</sub> (CO)Cl] <sup>+</sup>	100	3	3.2	3.8	
2	[Ru(bpy) <sub>2</sub> (CO)Cl] <sup>+</sup>	100	10	3.2	165	95
3	[Ru(bpy) <sub>2</sub> (CO)Cl] <sup>+</sup>	150	5	3.2	112	46
4	[Ru(bpy) <sub>2</sub> (CO)Cl] <sup>+</sup>	150	10	3.2	197	75
5	[Ru(bpy) <sub>2</sub> (CO)Cl] <sup>+</sup>	150	20	3.2	502	203
6	[Ru(bpy) <sub>2</sub> (CO)Cl] <sup>+</sup>	150	10	0	1.1	0.7
7	[Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	70	10	3.2	4.1	1.1
8	[Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	100	3	3.2	10.8	0.4
9	[Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	100	10	3.2	147	82.7
10	[Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	150	10	3.2	198	75
11	[Ru(bpy) <sub>3</sub> ] <sup>2+</sup> <sup>d</sup>	150	20	3.2	16	15

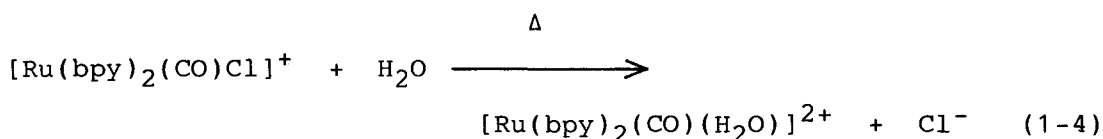
<sup>a</sup> PF<sub>6</sub><sup>-</sup> salt, 0.05 mmol in H<sub>2</sub>O (15 cm<sup>3</sup>). <sup>b</sup> Quantity of KOH initially added.

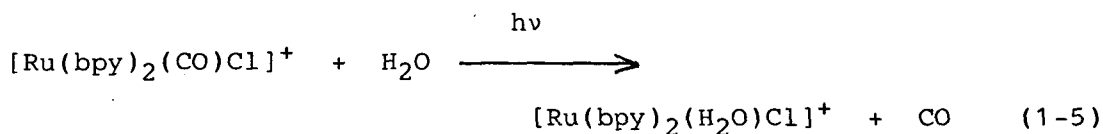
<sup>c</sup> Mol/(mol of catalyst, 20 h). <sup>d</sup> Cl<sup>-</sup> salt.

$(bpy)_3]Cl_2$  in the WGS reaction, however, is much lower than that of  $[Ru(bpy)_2(CO)Cl](PF_6)$  (compare entry 5 with 11, Table 1-I), suggesting that  $[Ru(bpy)_3]^{2+}$  is not the actual catalyst in the WGS reaction.

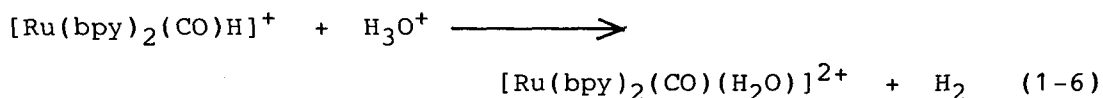
In the absence of KOH, the WGS reaction catalyzed by  $[Ru(bpy)_2(CO)Cl](PF_6)$  is slow even under 10 kg/cm<sup>2</sup> of CO at 150°C for 20 h (entry 6, Table 1-I); an almost colorless solution of the Ru(II) salt was obtained without any decomposition after the reaction for 20 h. The addition of  $NH_4PF_6$  to the resulting colorless solution afforded a known dicarbonyl complex,  $[Ru(bpy)_2(CO)_2](PF_6)_2$ ,<sup>13</sup> in a 70% yield. This complex isolated also catalyzes the WGS reaction under similar conditions (entries 7 - 10, Table 1-I); the turnover numbers at 100 and 150°C are essentially the same as those in the case with  $[Ru(bpy)_2(CO)Cl](PF_6)$  (compare entries 9 and 10 with 2 and 4, respectively, Table 1-I), indicating that  $[Ru(bpy)_2(CO)Cl]^+$  may be converted to  $[Ru(bpy)_2(CO)_2]^{2+}$  under CO pressure in an alkaline solution.

**Solvolysis of  $[Ru(bpy)_2(CO)Cl]^+$  to Give  $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ .** It has been suggested that  $[Ru(bpy)_2(CO)Cl]^+$  undergoes thermal and photochemical solvolyses in  $H_2O$  to give  $[Ru(bpy)_2(CO)(H_2O)]^{2+}$  (eq. 1-4) and  $[Ru(bpy)_2(H_2O)Cl]^+$  (eq. 1-5),





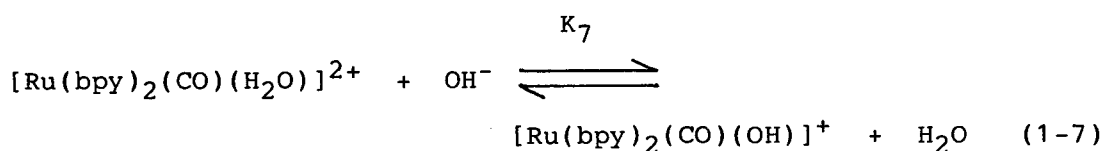
respectively.<sup>14</sup> However, there is no difference between the electronic absorption spectra of aqueous solutions of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$  after irradiation with a 500 W Xe lamp ( $\lambda > 360$  nm) at room temperature for 10 h and after refluxing for 1h. In addition, the spectra coincided with that of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$  formed in the reaction of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{H}](\text{PF}_6)$  with  $\text{H}_3\text{O}^+$  in water (pH 4.0) for 1 h at room temperature (eq. 1-6).<sup>9</sup> In



fact, the addition of  $\text{NaBPh}_4$  to the solution after the hydrolysis of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  afforded  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})](\text{BPh}_4)_2$  as a yellow precipitate. Thus,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  is subject to a thermal solvolysis in water to give  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$ , which may undergo the substitution of CO under CO pressures, yielding  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ .

**Interconversion between  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{OH})]^+$  in Weak Alkaline Solutions.** The addition of an aqueous KOH solution to a weak acidic solution of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$  resulted in the disappearance of electronic absorp-

tion bands of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$  ( $\lambda_{\text{max}}$  259, 304, 314, and 390 nm); instead of new bands appeared at 292, 350, and 444 nm with isosbestic points at 270, 304, and 340 nm, as shown in Figure 1-1. At pH values higher than 11, a limiting spectrum was obtained. In addition, the pH dependence of the spectra is reversible. Thus, an equilibrium may exist between  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{OH})]^+$  (eq. 1-7). The



equilibrium constant ( $K_7$ ) calculated from the change of the absorbance at 260 nm was  $5.06 \times 10^5 \text{ mol}^{-1} \text{ dm}^3$  at 25°C. The rate of the equilibrium reaction (eq. 1-7), however, is too fast to be determined by the stopped-flow method probably because of a diffusion controlled reaction. The existence of the equilibrium (eq. 1-7) is compatible with the fact that  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{OH})](\text{PF}_6)$  has been isolated on the addition of excess  $\text{NH}_4\text{PF}_6$  to a concentrated aqueous alkaline solution of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$ .

**Nucleophilic Attack of  $\text{OH}^-$  to CO Coordinated to  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ .** The electronic absorption spectrum of an aqueous solution of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  also changed reversibly depending on the pH value. The spectrum of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in an acidic solution shows two absorption maxima at 253 and 307 nm,

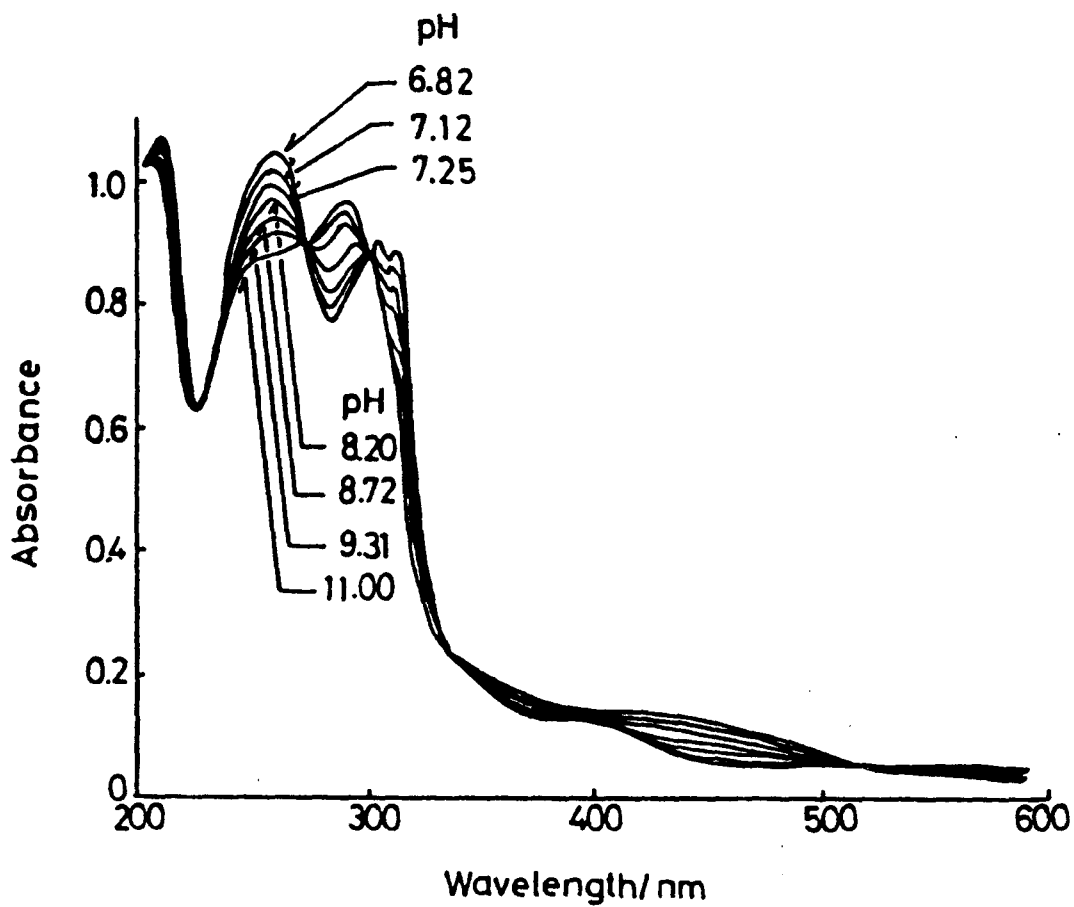
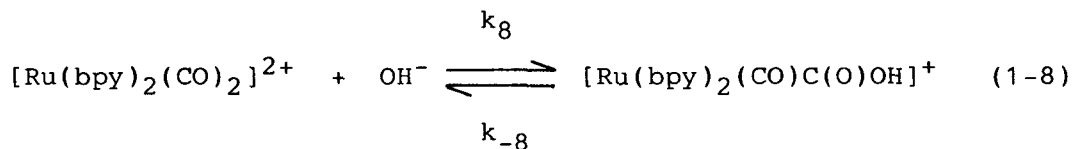


Figure 1-1. Electronic absorption spectra of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$  ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) in  $\text{H}_2\text{O}$  at various pH values ( $25^\circ\text{C}$ ).



whose intensities gradually decrease upon the addition of an aqueous KOH solution; instead four new bands at 248, 274, 344, and 430 nm occur with three isosbestic points at 260, 302, and 329 nm, as shown in Figure 1-2a. It should be noted, however, that in a weak alkaline medium there appears a weak shoulder at 400 nm, which is concealed by an absorption at 430 nm occurring at pH values higher than 9.0 (Figure 1-2b). The 430 nm band attained a maximum intensity around pH 11.0 and was almost unchanged at the higher pH values. Moreover,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  ( $5.15 \times 10^{-4} \text{ mol dm}^{-3}$ ) in  $\text{H}_2\text{O}$  behaves as a dibasic acid upon titration with an aqueous KOH solution ( $0.20 \text{ mol dm}^{-3}$ ), as shown in Figure 1-3. Thus, there may exist two successive equilibria in an aqueous alkaline solution of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ .

When an aqueous solution of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  with pH  $9.5 \pm 0.5$  was concentrated under reduced pressures, the ruthenium hydroxycarbonyl complex  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}](\text{PF}_6)$  was obtained as a yellow precipitate, suggesting that the nucleophilic attack of  $\text{OH}^-$  on CO of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  takes place in weak alkaline media. Thus,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  may exist as an equilibrium mixture with  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$  in weak alkaline solutions (eq. 1-8).



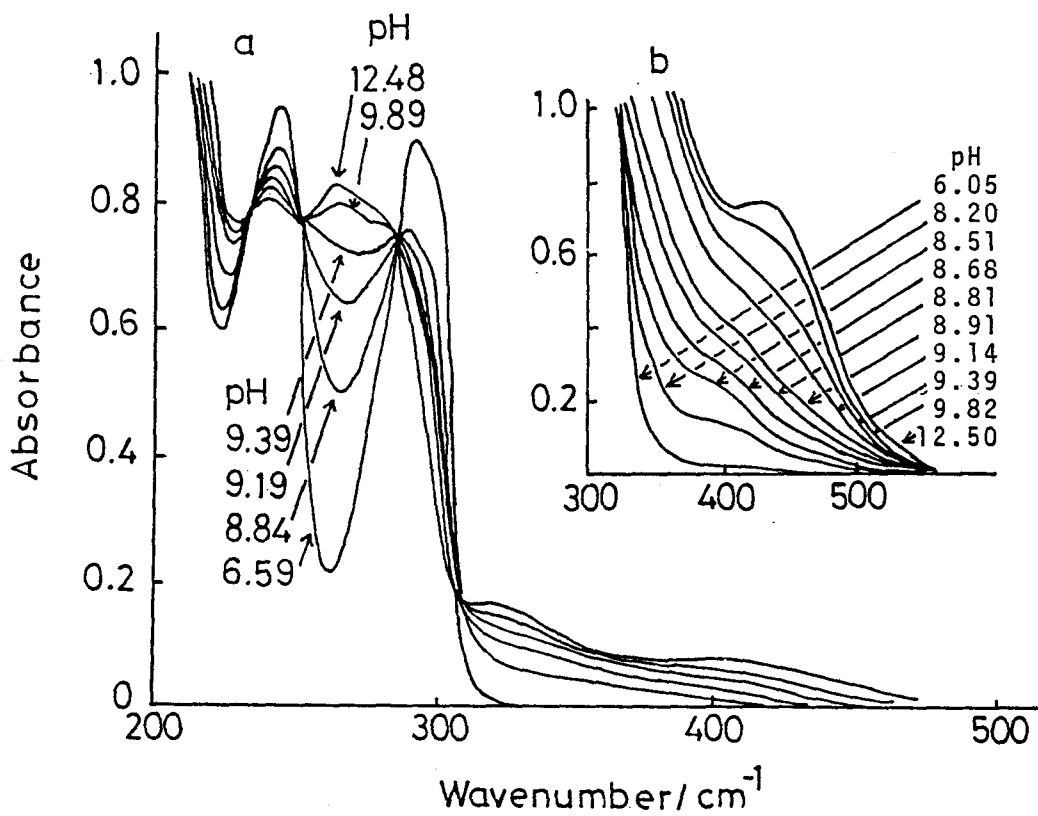


Figure 1-2. Electronic absorption spectra of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ , ((a)  $2.84 \times 10^{-5} \text{ mol dm}^{-3}$  and (b)  $2.84 \times 10^{-4} \text{ mol dm}^{-3}$ ) in  $\text{H}_2\text{O}$  at various pH values ( $25^\circ\text{C}$ ).

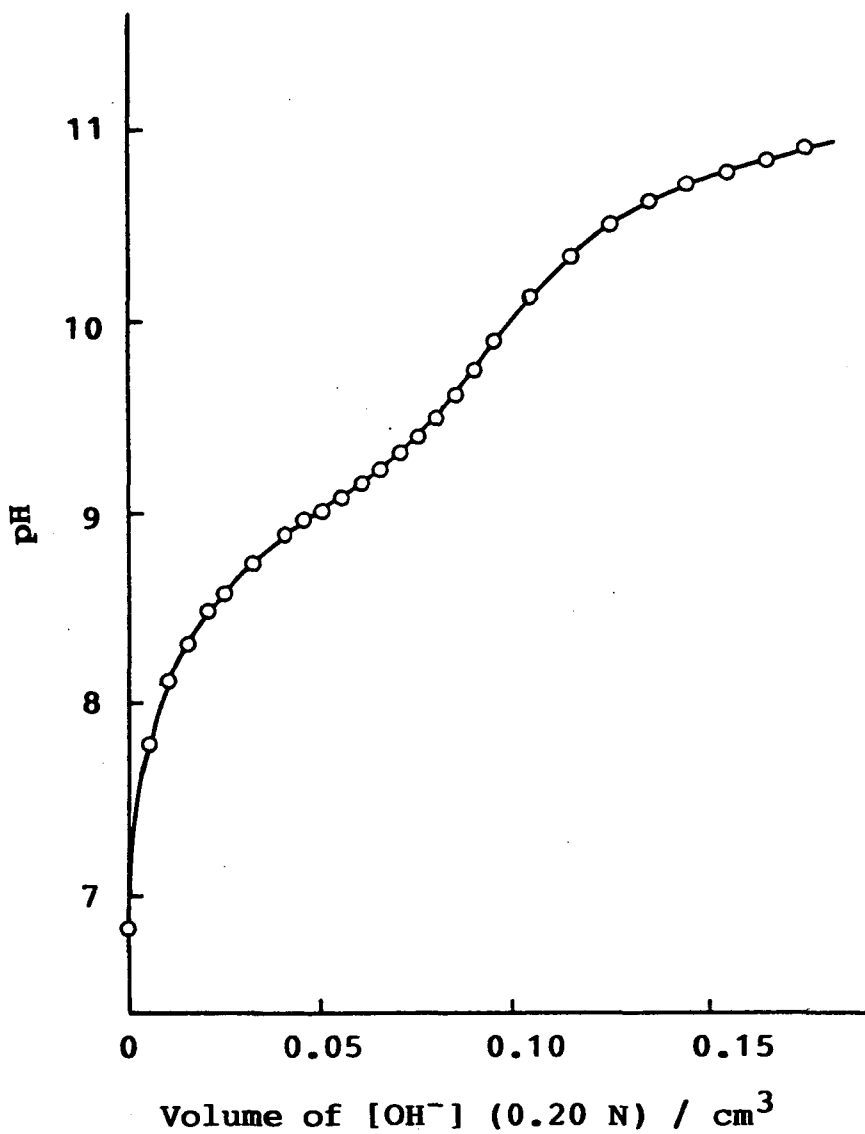
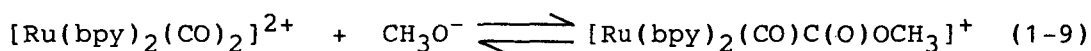
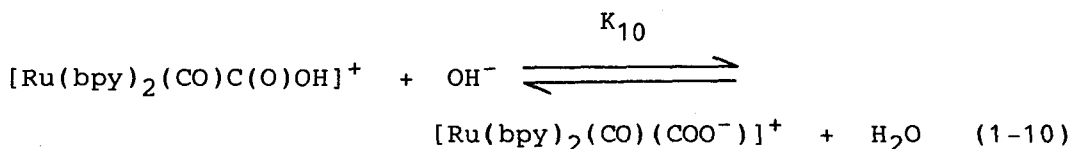


Figure 1-3. Titration of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  ( $1.03 \times 10^{-5}$  mol) in  $\text{H}_2\text{O}$  ( $20 \text{ cm}^3$ ) by an aqueous KOH solution ( $0.2 \text{ mol dm}^{-3}$ ) at  $25^\circ\text{C}$ .

The formation of the monohydroxycarbonyl complex from  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in alkaline solutions (eq. 1-8) may be consistent with the fact that the reaction of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  with  $\text{NaOCH}_3$  in dry  $\text{CH}_3\text{OH}$  afforded a monomethoxycarbonyl derivative,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OCH}_3](\text{PF}_6)$ , whose  $^1\text{H}$  nmr spectra shown in Figure 1-4 reveal that  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OCH}_3](\text{PF}_6)$  readily undergoes hydrolysis in the presence of a small amount of water to give  $\text{CH}_3\text{OH}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ . Thus,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OCH}_3]^+$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  may exist as an equilibrium mixture in solution, as expressed by eq. 1-9. A similar equilibrium is known for  $[\text{Ru}_3(\text{CO})_{11}\text{C}(\text{O})\text{OCH}_3]^-$ , which partly dissociates into  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{CH}_3\text{O}^-$  in methanol.<sup>15</sup>



The hydroxycarbonyl complex formed in eq. 1-8 is known to undergo deprotonation reactions in strong alkaline solutions.<sup>16</sup> Another equilibrium existing in alkaline solutions may, therefore, be expressed by eq. 1-10. The existence of the equilibria shown by eq. 1-8 and 1-10 may be consistent with the fact that the reaction of  $[\text{PtH}(\text{CO})(\text{P}(\underline{i}\text{-Pr})_3)_2]^+$  with an excess  $\text{KOH}$  in a mixture of  $\text{THF}$  and  $\text{H}_2\text{O}$  gives  $\text{PtH}(\text{COOK})(\text{P}(\underline{i}\text{-Pr})_3)_2$ .<sup>16</sup>



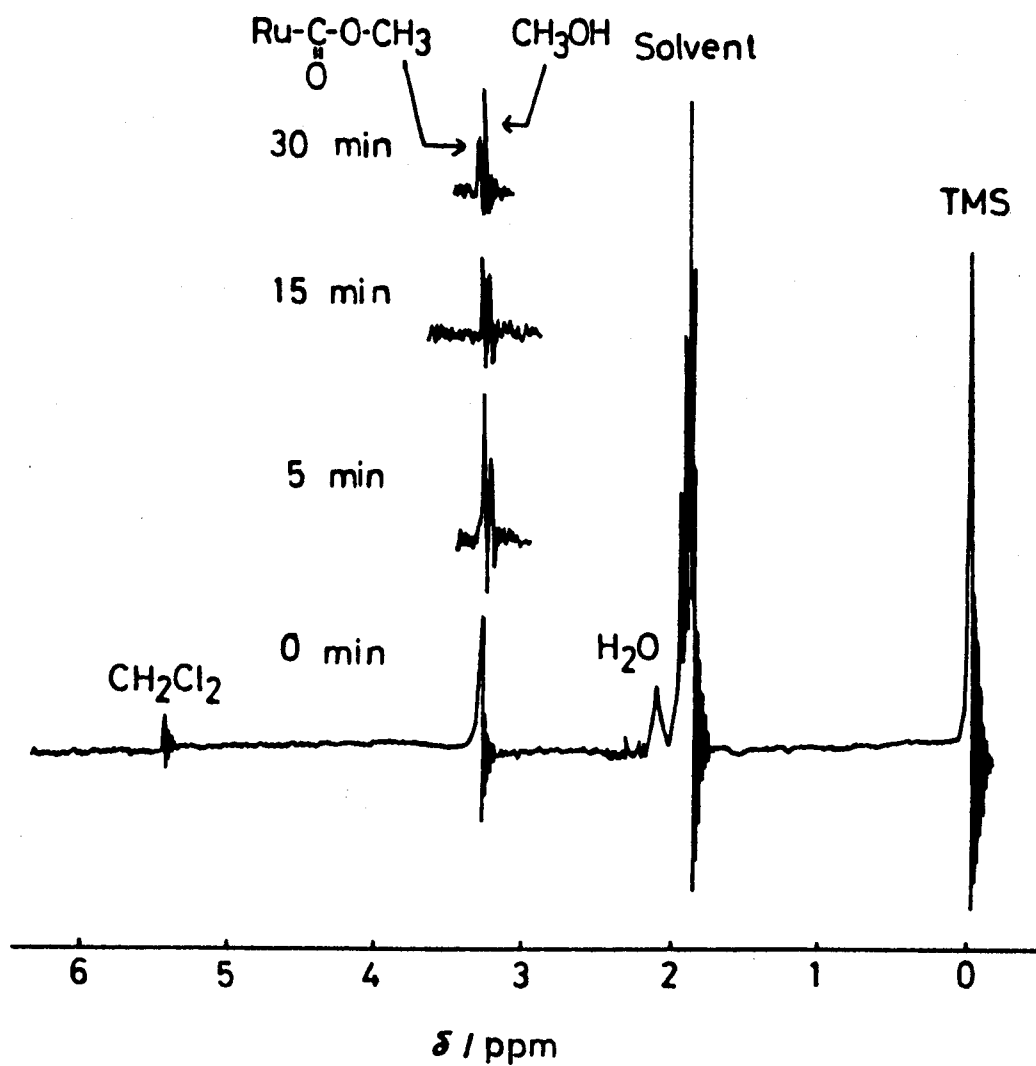


Figure 1-4. Time dependence of the  $^1\text{H}$  nmr spectrum of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OCH}_3](\text{PF}_6)$  after dissolved in  $\text{CD}_3\text{CN}$  containing a small amount of  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ . A  $\text{CH}_2\text{Cl}_2$  signal may be due to solvated molecules.

The equilibrium constants of eq. 1-8 ( $K_8 = k_8/k_{-8}$ ) and 1-10 ( $K_{10}$ ) were determined as  $1.32 \times 10^5$  and  $2.27 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$ , respectively, by the potentiometric method.<sup>17</sup> The rate of the reaction of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  with KOH at  $25^\circ\text{C}$ ,  $k_{\text{obsd}}$ , is plotted against the concentration of KOH, as shown in Figure 1-5, which indicates a linear relation between those quantities with a small nonzero intercept. The forward rate constant ( $k_8$ ) of eq. 1-8 determined from the slope of the plot is  $2.3 \times 10^4 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$ . The backward rate constant ( $k_{-8}$ ) was calculated as  $0.17 \text{ s}^{-1}$  from  $K_8$  and  $k_8$ , since the intercept of the plot (Figure 1-5) is too small to determine this value accurately. The reaction rate of eq. 1-10 has not been determined by the stopped-flow technique owing to a diffusion-controlled reaction.

**Distribution of the Ruthenium Species in Water.** In the WGS reaction under aqueous alkaline conditions, CO readily reacts with  $\text{OH}^-$  quantitatively to form a formate ion, which may function as a buffer to some extent, adjusting the pH of the initial solution around 8.5.<sup>12</sup> However, the pH value of the solution is lowered gradually to about 7.5 due to the formation of carbonate ion arising from  $\text{CO}_2$  evolved in the course of the WGS reaction.<sup>12</sup> Thus, the reaction in alkaline media actually proceeds in the pH range 7.5 - 8.5. The distribution of several Ru(II) species at various pH, calculated from the equilibrium constants  $K_7$ ,  $K_8$ , and  $K_{10}$ , are shown in Figure 1-6, which indicates that the Ru(II) species existing in the pH range of the present reaction (pH 7.5

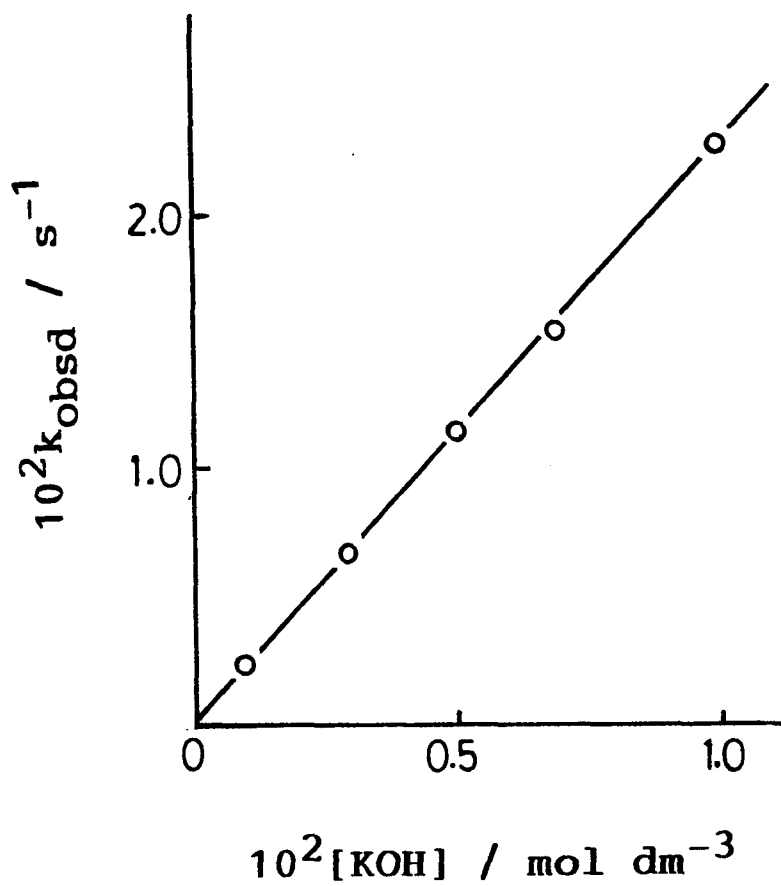


Figure 1-5. A plot of  $k_{\text{obsd}}$  vs.  $[\text{KOH}]$  for the reaction of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  with  $\text{KOH}$  in  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ .

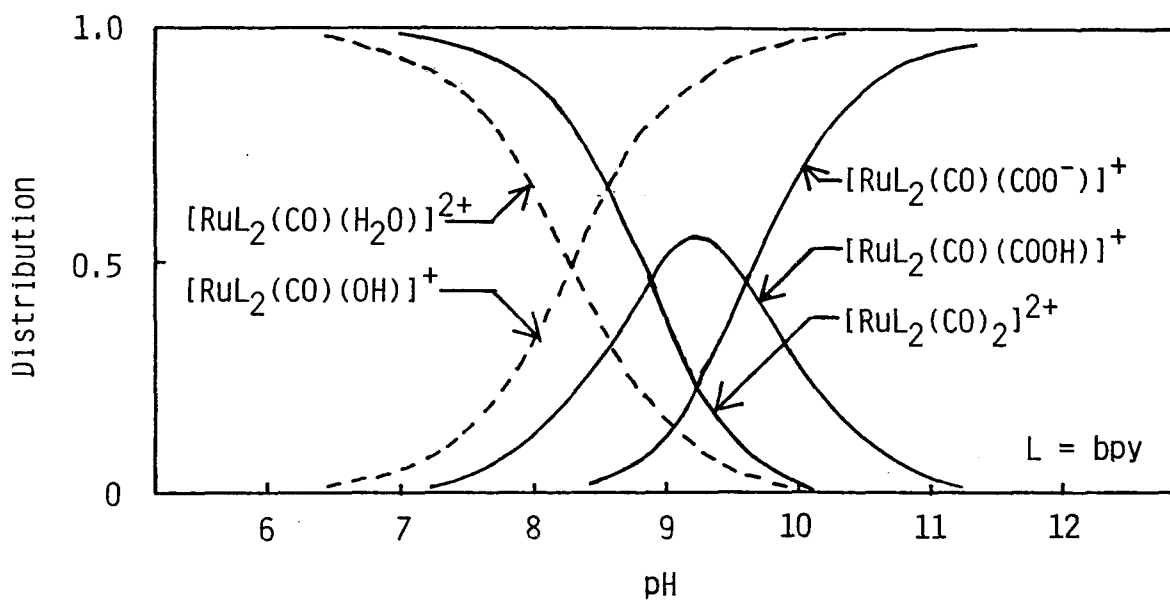


Figure 1-6. Distribution of the ruthenium species in  $\text{H}_2\text{O}$  at various pH at  $25^\circ\text{C}$ .



- 8.5) are  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ ,  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$ , and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{OH})]^+$ . Although a hydroxy-platinum complex,  $\text{Pt}(\text{CH}_3)(\text{OH})\text{L}$  ( $\text{L} = \text{bis}(\text{tertiary phosphine})$ ), has been reported to undergo an insertion reaction of  $\text{CO}$ , affording the hydroxycarbonyl derivatives  $\text{Pt}(\text{CH}_3)(\text{C}(\text{O})\text{OH})\text{L}$ ,<sup>18</sup> a substitution reaction of  $\text{CH}_3\text{CN}$ , but not  $\text{CO}$ , for the hydroxy group of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{OH})](\text{PF}_6)$  occurred when the hydroxyruthenium(II) complex was heated in  $\text{CH}_3\text{CN}$  under  $10 \text{ kg/cm}^2$  of  $\text{CO}$  at  $100^\circ\text{C}$ .

**The Decarboxylation of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ .** When an aqueous solution of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  at pH 8.09 ( $\text{KOH}-\text{H}_3\text{BO}_3$  buffer) was kept at  $100^\circ\text{C}$  for 2 h under  $10 \text{ kg/cm}^2$  of  $\text{N}_2$  in a bomb,  $\text{CO}_2$  and  $\text{H}_2$  were evolved. To the resulting solution was added an aqueous solution of  $\text{NaBPh}_4$  to precipitate all the cationic ruthenium species<sup>19</sup> as the  $\text{BPh}_4^-$  salt. After collected by filtration, washed with water, and dried in vacuo, the precipitate in Nujol mulls exhibits four IR bands at 1910 (s), 1960 (m), 1980 (s), and 1990 (sh)  $\text{cm}^{-1}$  due to  $\nu(\text{C}\equiv\text{O})$ , as shown in Figure 1-7. The former two bands are assigned to  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{H}](\text{BPh}_4)$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}](\text{BPh}_4)$ , respectively, by comparing the frequencies with those of the authentic samples. Of the latter two, the intense band is associated with  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})](\text{BPh}_4)_2$  and the shoulder is assignable to  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{OH})](\text{BPh}_4)$ , based on the infrared spectra of the authentic samples. On the other hand, no appreciable thermolysis of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  has taken place when an aqueous solution (pH

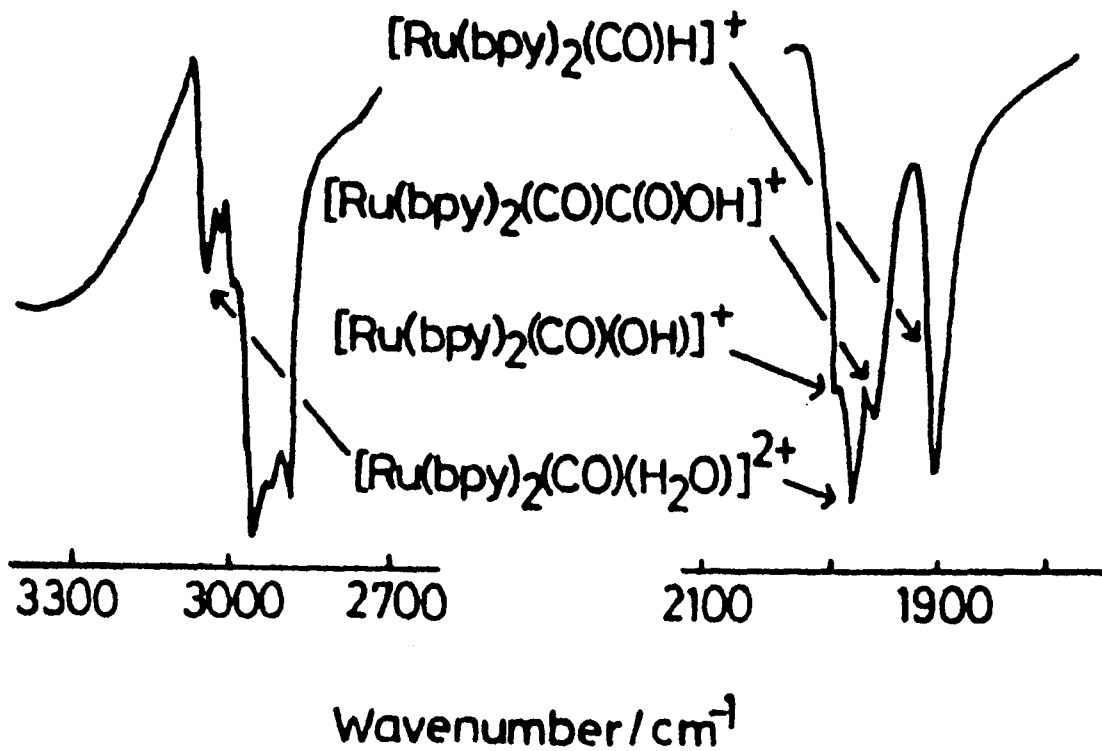
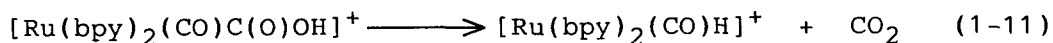


Figure 1-7. Infrared absorption spectra of the thermolysis products of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  in  $\text{H}_2\text{O}$  (pH 8.09) at  $100^\circ\text{C}$ .

11.0, KOH-H<sub>3</sub>PO<sub>4</sub> buffer) of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was heated at 100°C for 2 h under 10 kg/cm<sup>2</sup> of N<sub>2</sub>.<sup>20</sup> These results indicate that [Ru(bpy)<sub>2</sub>(CO)C(O)OH]<sup>+</sup> existing as an equilibrium mixture with [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in a weak aqueous alkaline solution undergoes decarboxylation to give [Ru(bpy)<sub>2</sub>(CO)H]<sup>+</sup> (eq. 1-11), which



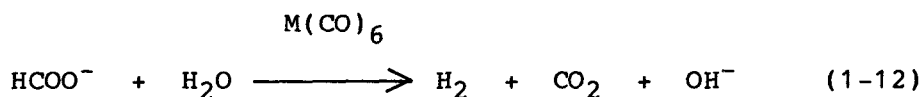
further reacts with H<sub>3</sub>O<sup>+</sup> to produce H<sub>2</sub> and [Ru(bpy)<sub>2</sub>(CO)(H<sub>2</sub>O)]<sup>2+</sup> (eq. 1-6), as described in the previous section. In fact, the hydrolysis of [Ru(bpy)<sub>2</sub>(CO)H](PF<sub>6</sub>) in water at pH 8.05 (KOH-H<sub>3</sub>BO<sub>3</sub> buffer) under 10 kg/cm<sup>2</sup> of N<sub>2</sub> at 100°C has evolved H<sub>2</sub>. The reaction of [Ru(bpy)<sub>2</sub>(CO)H]<sup>+</sup> with H<sub>2</sub>O in place of H<sub>3</sub>O<sup>+</sup> may also produce H<sub>2</sub> together with [Ru(bpy)<sub>2</sub>(CO)(OH)]<sup>+</sup>, though the contribution of this reaction to the H<sub>2</sub> formation has not been evaluated because of a rapid equilibrium between [Ru(bpy)<sub>2</sub>(CO)(H<sub>2</sub>O)]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)(OH)]<sup>+</sup> in weak alkaline solutions. However, [Ru(bpy)<sub>2</sub>(CO)H]<sup>+</sup> may be one of the actual catalyst in the reaction, since [Ru(bpy)<sub>2</sub>(CO)H](PF<sub>6</sub>) as a catalyst in the presence of KOH under 10 kg/cm<sup>2</sup> of CO at 100°C for 20 h gave the turnover number 179, which is essentially the same value as that with [Ru(bpy)<sub>2</sub>(CO)Cl](PF<sub>6</sub>) under the same conditions (entry 2 in Table 1-I).

#### **The WGS Reaction Using Ru(bpy)<sub>2</sub>Cl<sub>2</sub> as a Catalyst Precursor.**

It has been reported that Ru(bpy)<sub>2</sub>Cl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> under CO

pressures at 80°C is converted to  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ .<sup>13</sup> The same reaction occurred also when  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (0.05 mmol) was allowed to stand under 10 kg/cm<sup>2</sup> of CO at 100°C in water (15 cm<sup>3</sup>) for 20 h.<sup>21</sup> As expected from this result, a large turnover number (243) was obtained in the WGS reaction using  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (0.05 mmol) as a catalyst precursor in the presence of KOH (3.2 mmol) under 10 kg/cm<sup>2</sup> of CO at 100°C for 20 h. It should be noted that the turnover number is considerably larger than that obtained in the reaction using the  $\text{PF}_6^-$  salt of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  or  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  (see entry 2 or 9, Table 1-I). On the other hand, the addition of  $\text{NH}_4\text{PF}_6$  (0.10 mmol) to an aqueous solution containing  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (0.05 mmol) and KOH (3.2 mmol) under 10 kg/cm<sup>2</sup> of CO at 100°C has decreased the turnover number of the reaction to 149. This result may be interpreted by a weak poisoning effect of  $\text{PF}_6^-$  on the WGS reaction.

**Catalytic Cycle of the WGS Reaction.** The WGS reaction catalyzed by some metal carbonyls,  $\text{M}(\text{CO})_6$  (M = Cr, Mo, W), in alkaline media has been reported to proceed preferentially by decomposition of the formate ion (eq. 1-12) which is produced at

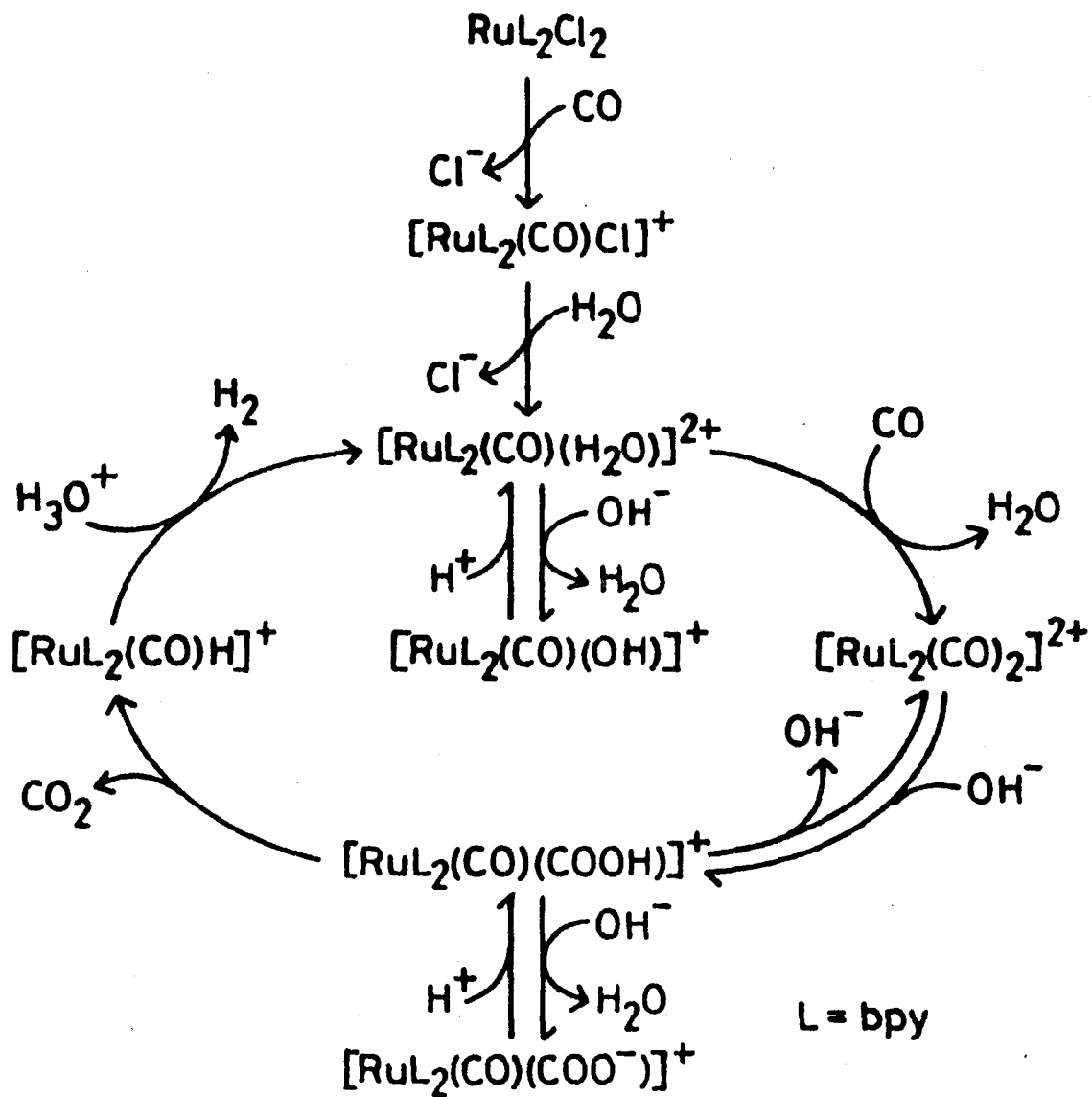


the beginning of the reaction.<sup>22-24</sup> For example,  $\text{HCOO}^-$  reacts with  $\text{M}(\text{CO})_5$  resulting from the dissociation of a CO ligand of

$M(CO)_6$  to afford  $M(CO)_5OC(O)H^-$ , which undergoes decarboxylation to generate  $M(CO)_5H^-$ , as proposed by King et al.<sup>23,25,26</sup> A similar thermal decarboxylation has been reported for  $[Ru(bpy)_2(CO)OC(O)H]^+$  in 2-methoxyethanol, giving  $[Ru(bpy)_2(CO)H]^+$ .<sup>27,28</sup> Therefore, we have examined the  $H_2$  evolution arising from the decomposition of  $HCOO^-$  in the presence of the Ru(II) complexes. The thermal decomposition of  $HCOOH$  (13 mmol) in the presence of  $[Ru(bpy)_2(CO)X](PF_6)$  ( $X = H, Cl$ ) (0.05 mmol) in  $H_2O$  at pH 8.0 - 9.0 (KOH- $HCOOH$  buffer) evolved 0.5 - 1.0 mmol of  $H_2$  under 10  $kg/cm^2$  of  $N_2$  at  $100^\circ C$  for 20 h. The amount of  $H_2$  evolved, however, was much smaller than that in the WGS reaction at  $100^\circ C$  (see entries 2 and 9 in Table 1-I), despite the presence of a large amount of  $HCOO^-$  in the solution. Thus, the decomposition of  $HCOOH$  may be no main pathway for the  $H_2$  evolution in the present WGS reaction.

A plausible catalytic cycle of the reaction is depicted in Scheme 1-I;  $Ru(bpy)_2Cl_2$  in an aqueous KOH solution under CO pressures at elevated temperatures may be converted to  $[Ru(bpy)_2(CO)_2]^{2+}$  probably through  $[Ru(bpy)_2(CO)Cl]^+$  and  $[Ru(bpy)_2(CO)(H_2O)]^{2+}$  successively, followed by the substitution reaction by CO. The nucleophilic attack of  $OH^-$  to one of the coordinated CO of  $[Ru(bpy)_2(CO)_2]^{2+}$  at pH 8.0 - 9.0 affords  $[Ru(bpy)_2(CO)C(O)OH]^+$ , which undergoes the decarboxylation to give  $[Ru(bpy)_2(CO)H]^+$ . The hydride complex thus formed reacts with  $H_3O^+$  to evolve  $H_2$  with regenerating  $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ , while the reaction of  $[Ru(bpy)_2(CO)H]^+$  with  $H_2O$  may participate into the

Scheme 1-I



production of H<sub>2</sub> to some extent. These reaction pathways are strongly supported by the isolation or characterization of all the intermediates.

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- (20) The final solution was treated with  $\text{HCl}$  to regenerate  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ , which was confirmed by the electronic absorption spectrum.
- (21) A crude product obtained by evaporation of the solvent water

was  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  contaminated with a small amount of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})]^{2+}$ , as confirmed by the infrared spectrum.

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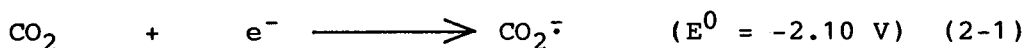
## Chapter 2

### Electrochemical CO<sub>2</sub> Reduction Catalyzed by Ruthenium Complexes; the Effect of pH on the Formation of CO and HCOO<sup>-</sup>

#### 2-1 Introduction

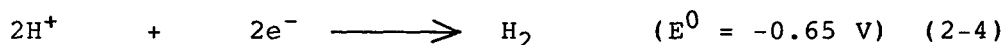
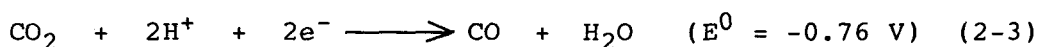
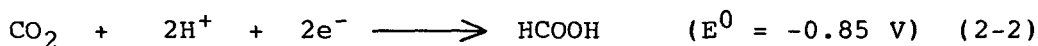
Effective utilization of CO<sub>2</sub> being an ultimate oxidation product of organic molecule has become one of the most important subjects in the field of chemistry to cope with a predictable oil shortage in near future and the recent problem of increasing CO<sub>2</sub> concentration in air. Along this line, electrochemical,<sup>1-10</sup> photochemical,<sup>11-16</sup> and thermal<sup>17-21</sup> reductions of CO<sub>2</sub> have been studied by using homogeneous catalysts. Of these, the electrochemical reduction of CO<sub>2</sub> seems to have a bright prospect compared with other methods, since the reaction can easily be controlled by changing the applied potentials.

Electrochemically direct reduction of CO<sub>2</sub> giving CO<sub>2</sub><sup>-</sup> requires more negative potentials than -2.10 V vs. SCE (eq. 2-1).<sup>10</sup> However, CO<sub>2</sub> can be reduced at more positive potentials



when protons participate in the reduction. The equilibrium potentials of the redox reactions affording HCOOH and CO (eq. 2-2

and 2-3, respectively) are -0.85 and -0.76 V vs. SCE, respectively, in water at pH 7.0.<sup>11</sup> These values are somewhat more negative than the redox potential of the H<sub>2</sub>/H<sup>+</sup> couple at pH 7.0 (eq. 2-4).<sup>11</sup> In order to depress the evolution of H<sub>2</sub> in the



course of reduction of CO<sub>2</sub>, therefore, it is desirable to use any catalysts which have a strong affinity for CO<sub>2</sub> even in the presence of protons. Of a number of transition-metal complexes as catalysts for the reduction of CO<sub>2</sub>, nickel, rhenium, and ruthenium complexes have especially been of much interest from the viewpoint of efficiency for the formation of CO, HCOO<sup>-</sup>, or both.

This chapter describes the electrochemical CO<sub>2</sub> reduction catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup> which are catalysts for WGS reactions, in H<sub>2</sub>O/DMF mixtures with different pH values.

## 2-2 Experimental Section

**Materials.** [Ru(bpy)<sub>2</sub>(CO)Cl](PF<sub>6</sub>),<sup>22</sup> [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]-

$(PF_6)_2$ ,<sup>22</sup> and  $Ru(bpy)_2Cl_2 \cdot 2H_2O$ ,<sup>23</sup> were prepared according to the literatures. Commercially available guaranteed reagent grades of LiCl, NaOH,  $H_3PO_4$ ,  $NaHCO_3$ ,  $Na_2CO_3$ , and  $NBu^n_4OH$  were used without further purification.  $NBu^n_4ClO_4$  prepared by the reaction of  $NBu^n_4Br$  with  $HClO_4$  in water was recrystallized five times from diethyl ether/acetone. N,N-Dimethylformamide (DMF) was purified by refluxing with CaO for 24 h, followed by distillation under reduced pressure, and stored under an  $N_2$  atmosphere. Mercury used as a working electrode was washed with aqueous HCl and aqueous  $NaBH_4$  successively, and then distilled under reduced pressures.

**Physical Measurements.** Electrochemical measurements were carried out in a pyrex cell (30 or 100  $cm^3$ ) equipped with a hanging mercury drop electrode (HMDE, Metrohm Model E-410), a Pt auxiliary electrode, a saturated calomel electrode (SCE), and a nozzle for bubbling  $N_2$  or  $CO_2$ . Cyclic voltammograms were obtained by the use of a Hokuto Denko HA-301 potentiostat, a Hokuto Denko HB-107A function generator, and a Yokogawa Electric Inc. 3077 X-Y recorder. The surface area of the HMDE was maintained at  $2.22 \pm 0.07 \text{ mm}^2$  throughout the work. Electronic absorption spectra were measured with a Union SM-401 spectrophotometer. Spectroelectrochemical experiments were carried out by the use of an optically transparent thin-layer electrode (OTTLE) cell, consisting of a Pt-gauze electrode in a 0.5 mm quartz cuvette, a Pt-wire auxiliary electrode, and a saturated

calomel reference electrode (SCE).<sup>24</sup>

**Electrochemical Reduction of CO<sub>2</sub>.** The reduction of CO<sub>2</sub> in a CO<sub>2</sub>-saturated H<sub>2</sub>O/DMF mixture containing [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> or [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup> was carried out by the controlled potential electrolysis at -1.50 V vs. SCE on an Hg electrode. The electrolysis cell<sup>25</sup> as depicted in Figure 2-1 was consisted of three compartments; one for an Hg working electrode (3.1 cm<sup>2</sup>), the second separated from the working electrode cell by a glass frit for a platinum auxiliary electrode (ca. 3 cm<sup>2</sup>), and the third for an SCE reference electrode. The volume of these compartments were 35, 25, and 8 cm<sup>3</sup>, respectively, and the former two were connected with volumetric flasks with stainless tubes (I. D. = 0.4 mm). CO<sub>2</sub>-saturated H<sub>2</sub>O/DMF solutions containing [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> or [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup> (0.50 mmol dm<sup>-3</sup>, 50 cm<sup>3</sup>) were prepared by mixing a CO<sub>2</sub>-saturated DMF solution containing either the Ru(II) complex (0.025 mmol, 5 - 45 cm<sup>3</sup>) with CO<sub>2</sub>-saturated water (pH 6.0 or 9.5, 5 - 45 cm<sup>3</sup>) buffered with H<sub>3</sub>PO<sub>4</sub>-NaOH (ionic strength is 0.05). After a stream of CO<sub>2</sub> was passed from the working electrode compartment to the volumetric flask for 30 min to displace the air in the electrolysis cell, the CO<sub>2</sub>-saturated H<sub>2</sub>O/DMF solution (40 cm<sup>3</sup>) containing [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> or [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup> was injected through a septum cap attached to the top of the working electrode compartment by a syringe technique. Then, the electrolysis cell was placed in a thermostat at 30 ± 0.1°C and the solution was stirred magnetically for 1 h. Attain-

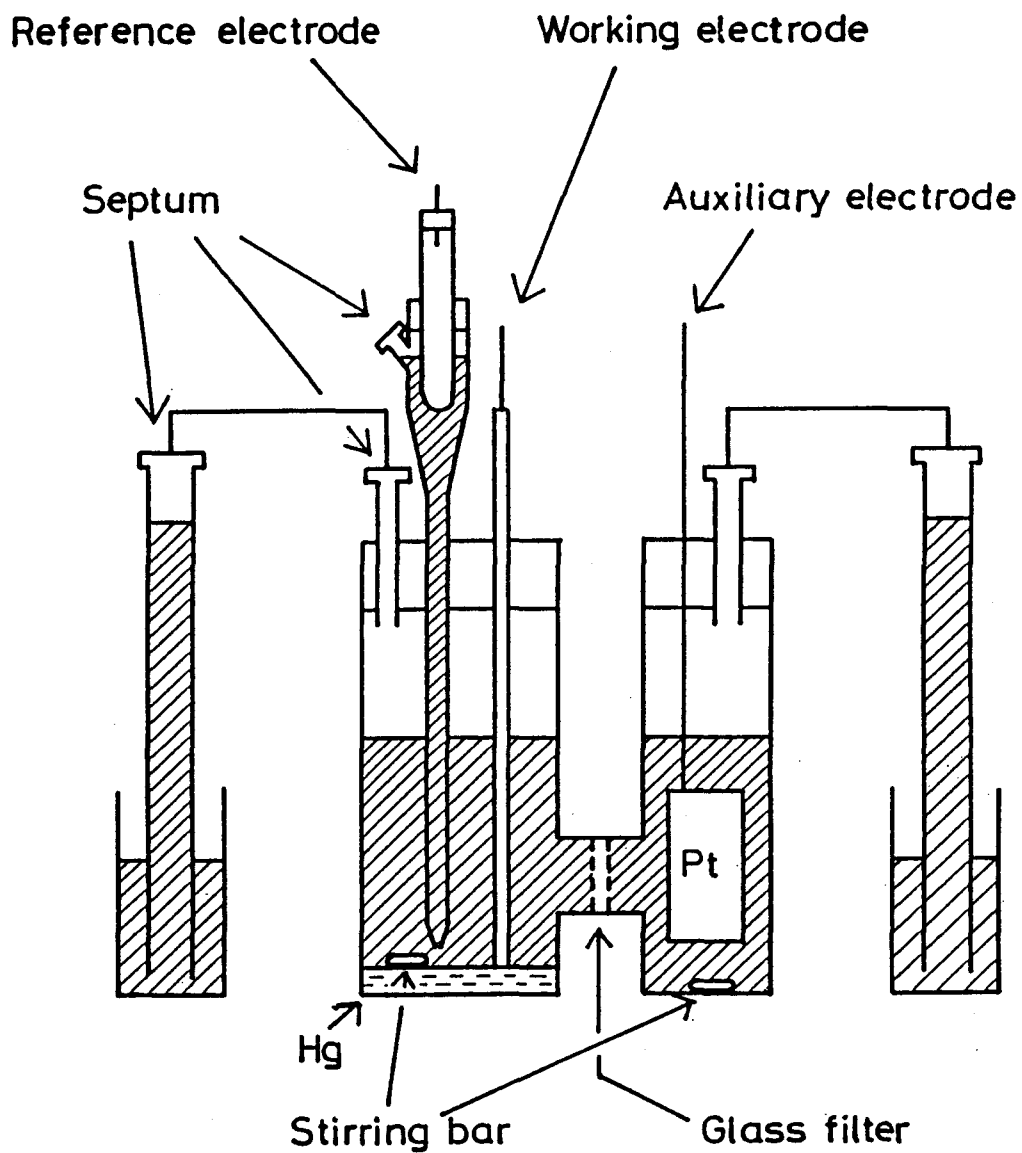


Figure 2-1. The electrolysis cell.

ment of the thermal equilibrium of  $\text{CO}_2$  between the gaseous and liquid phase in the cell was confirmed from a constant height of the meniscus of  $\text{CO}_2$ -saturated water in the volumetric flasks connected with the working and auxiliary electrode compartments. The reduction of  $\text{CO}_2$  was started by applying a given electrolysis potential to an Hg working electrode with a potentiostat, and the number of coulombs consumed in the reduction was measured with a Hokuto Denko Model HF-201 coulomb meter.

**Product Analysis.** At a fixed interval of coulombs consumed in the reduction, each  $0.1 \text{ cm}^3$  portion of gas was sampled from the gaseous phases both of the working electrode compartment and of the volumetric flask with a pressure-locked syringe (Precision Sampling). Gaseous products were analyzed on a Shimadzu GC-3BT gas chromatograph equipped with a 2 m column filled with Molecular Sieve 13X using He as a carrier gas (for the determination of CO) and on a Shimadzu GC-7A gas chromatograph equipped with a 2 m column filled with Unibeads 1S using  $\text{N}_2$  as a carrier gas (for the determination of  $\text{H}_2$  and  $\text{CO}_2$ ). The volume of the gas evolved in the reduction was determined by change of the meniscus in the volumetric flask connected with the working electrode compartment. The analysis of the solution was performed by sampling each  $0.1 \text{ cm}^3$  portion from the working electrode compartment through a septum cap by a syringe technique at a fixed interval of coulombs consumed. The amount of  $\text{HCOO}^-$  produced in the solution was determined with a Shimadzu Isotacho-



phoretic Analyzer IP-2A using aqueous  $\text{Cd}(\text{NO}_3)_2$  ( $6.0 \text{ mmol dm}^{-3}$ ) and caproic acid ( $10.0 \text{ mmol dm}^{-3}$ ) solutions as leading and terminal electrolytes, respectively.

## 2-3 Results and Discussion

### Cyclic Voltammetry of the Ruthenium Bipyridyl Complexes.

Figure 2-2 shows the cyclic voltammograms of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  by using a hanging mercury drop electrode (HMDE) with the surface area of  $2.22 \pm 0.07 \text{ mm}^2$  in DMF under  $\text{N}_2$  and  $\text{CO}_2$  atmospheres. The cyclic voltammogram of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  in an  $\text{N}_2$ -saturated DMF solution shows two redox couples in the potential range  $-0.50 \text{ V}$  to  $-1.60 \text{ V vs. SCE}$ . (a solid line in Figure 2-2a). The peak separations between the cathodic and anodic waves of the redox reactions at  $E_{1/2} = -1.21$  and  $-1.41 \text{ V vs. SCE}$  are  $60 \text{ mV}$  and  $90 \text{ mV}$ , respectively, at the sweep rate  $0.10 \text{ V s}^{-1}$ . The peak potential of the former couple was independent of the sweep rate in the range  $0.50$  to  $0.05 \text{ V s}^{-1}$ . On the other hand, the anodic wave of the latter couple almost disappeared at the sweep rate  $0.05 \text{ V s}^{-1}$ , while the corresponding cathodic wave still observed clearly at  $-1.48 \text{ V vs. SCE}$ . Thus,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  undergoes two successive one-electron reductions; one is reversible reduction at  $-1.24 \text{ V}$  and the other essentially an irreversible reduction around  $-1.48 \text{ V vs. SCE}$ , confirming that the two-electron reduction of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  is followed by a slow chemical reaction.

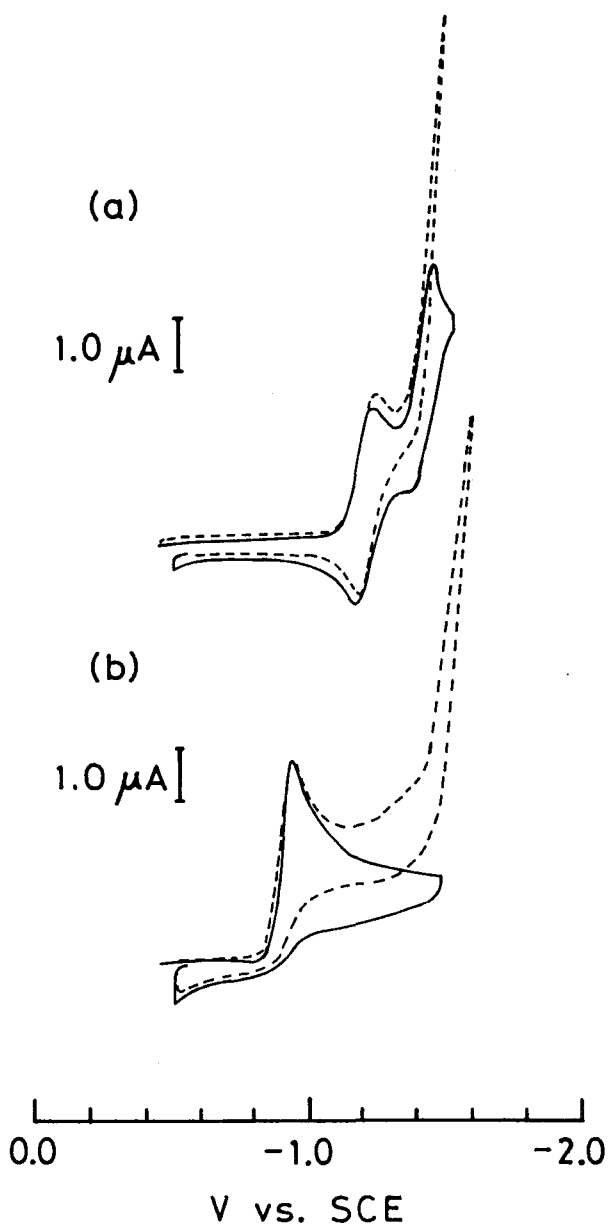


Figure 2-2. Cyclic voltammograms of (a)  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  and (b)  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) in DMF containing  $\text{NBu}^n_4\text{ClO}_4$  ( $0.10 \text{ mol dm}^{-3}$ ) as a supporting electrolyte under  $\text{N}_2$  (—) and  $\text{CO}_2$  (---) atmosphere, using an Hg electrode (sweep rate =  $0.10 \text{ V s}^{-1}$ ).

The cyclic voltammogram of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  under  $\text{N}_2$  atmosphere shows an irreversible cathodic wave at  $-0.95 \text{ V vs. SCE}$  at the sweep rate  $0.10 \text{ V s}^{-1}$  (a solid line in Figure 2-2b). If one assumes that the diffusion constant of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  is essentially identical with that of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  on the basis of their similar structures, the number of electrons consumed in the irreversible cathodic wave of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  at  $-0.95 \text{ V}$  can be determined by using the diffusion constant of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  calculated from the reversible cathodic wave at  $-1.24 \text{ V vs. SCE}$ . The diffusion constant of an electroactive species which undergoes a reversible redox reaction can be correlated with its peak current ( $i_p$ ) in the cyclic voltammogram at  $25^\circ\text{C}$  as expressed by eq. 2-5,<sup>26</sup>

$$i_p(\text{rev}) = (2.69 \times 10^5) n^{3/2} A D_0^{1/2} v^{1/2} C_0^* \quad (2-5)$$

where  $n$ ,  $A$ ,  $D_0$ ,  $v$ , and  $C_0^*$  are the number of electrons consumed in the redox reaction, the surface area ( $\text{cm}^2$ ) of an electrode, the diffusion constant ( $\text{cm}^2 \text{ s}^{-1}$ ) of an electroactive species, a voltage sweep rate ( $\text{V s}^{-1}$ ), and the bulk concentration ( $\text{mol cm}^{-3}$ ) of an electroactive species, respectively. Thus, the diffusion constant of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  is determined as  $3.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  from the peak current  $2.3 \times 10^{-6} \text{ A}$  of the one-electron reversible cathodic wave at the sweep rate  $0.20 \text{ V s}^{-1}$ .<sup>27</sup> On the other hand, the relationship between the peak current  $i_p(\text{irr})$  and the diffusion constant  $D_0$  of an electroactive species which undergoes a

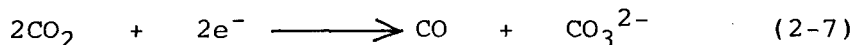
totally irreversible redox reaction, can be expressed by eq. 2-6,<sup>28</sup>

$$i_p(\text{irr}) = (2.99 \times 10^5) n \left( \frac{47.7}{|E_p - E_{p/2}|} \right)^{1/2} \cdot A \cdot D_0^{1/2} \cdot v^{1/2} \cdot C_0^* \quad (2-6)$$

where  $E_p$  and  $E_{p/2}$  are the peak potential (mV) of an irreversible wave and the potential (mV) at  $i_p/2$ , respectively. The values of  $|E_p - E_{p/2}|$  and  $i_p(\text{irr})$  of the irreversible cathodic wave of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  at the sweep rate  $0.20 \text{ V s}^{-1}$  were calculated as 60 mV and  $4.5 \times 10^{-6} \text{ A}$ , respectively. Substitution of these values in eq. 2-6 yields  $n = 1.96$ . Thus,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  undergoes an irreversible two-electron reduction around  $-0.95 \text{ V}$ .

The cyclic voltammograms of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in  $\text{CO}_2$ -saturated DMF (dashed lines in Figures 2-2a and 2b, respectively) are essentially the same as those of the corresponding complexes in  $\text{N}_2$ -saturated DMF, except that strong cathodic currents begin to flow around  $-1.40 \text{ V vs. SCE}$  in  $\text{CO}_2$ -saturated DMF (compare solid lines and dashed lines in Figures 2-2a and 2b). Removal of  $\text{CO}_2$  from  $\text{CO}_2$ -saturated DMF solutions of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  by bubbling  $\text{N}_2$  through the solution for 1 h resulted in complete disappearance of the strong cathodic currents to give the cyclic voltammograms of those complexes in  $\text{N}_2$ -saturated DMF solutions. Thus, in the presence of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  or  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ,  $\text{CO}_2$  can be reduced at  $-1.40 \text{ V vs. SCE}$ .

**Electrochemical Reduction of CO<sub>2</sub>.** The controlled potential electrolysis of a CO<sub>2</sub>-saturated anhydrous DMF solution containing NBu<sup>n</sup><sub>4</sub>ClO<sub>4</sub> as a supporting electrolyte and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> as a catalyst at -1.50 V vs. SCE has resulted in decomposition of the complex to yield a black precipitate with liberation of only about 10% on the basis of the amount of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>.<sup>29</sup> However, the same electrolysis of a CO<sub>2</sub>-saturated H<sub>2</sub>O/DMF (1:1, v/v) solution containing LiCl (0.10 mol dm<sup>-3</sup>) as a supporting electrolyte and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> (5.0 x 10<sup>-4</sup> mol dm<sup>-3</sup>) catalytically produces HCOO<sup>-</sup> and CO (eqs. 2-2 and 2-3) together with a little amount of H<sub>2</sub> (eq. 2-4), as shown in Figure 2-3. This result is in contrast to the catalytic reduction of CO<sub>2</sub> by the electrochemically (-1.50 V vs. SCE) reduced species Re(bpy)(CO)<sub>3</sub>Cl in CO<sub>2</sub>-saturated CH<sub>3</sub>CN, where the reduction of CO<sub>2</sub> takes place according to eq. 2-7.<sup>2</sup> Thus, the present CO<sub>2</sub> reduction does not result from an oxide transfer reaction shown in eq. 2-7.



As shown in Figure 2-3, the amount of CO formed increases linearly with the number of coulombs consumed in the reaction of CO<sub>2</sub> up to 60 coulombs, and thereafter the rate of CO evolution gradually decreases. On the other hand, the amount of HCOO<sup>-</sup> formed slowly increases during the consumption of initial 60 coulombs and thereafter rapidly increases. The turnover numbers

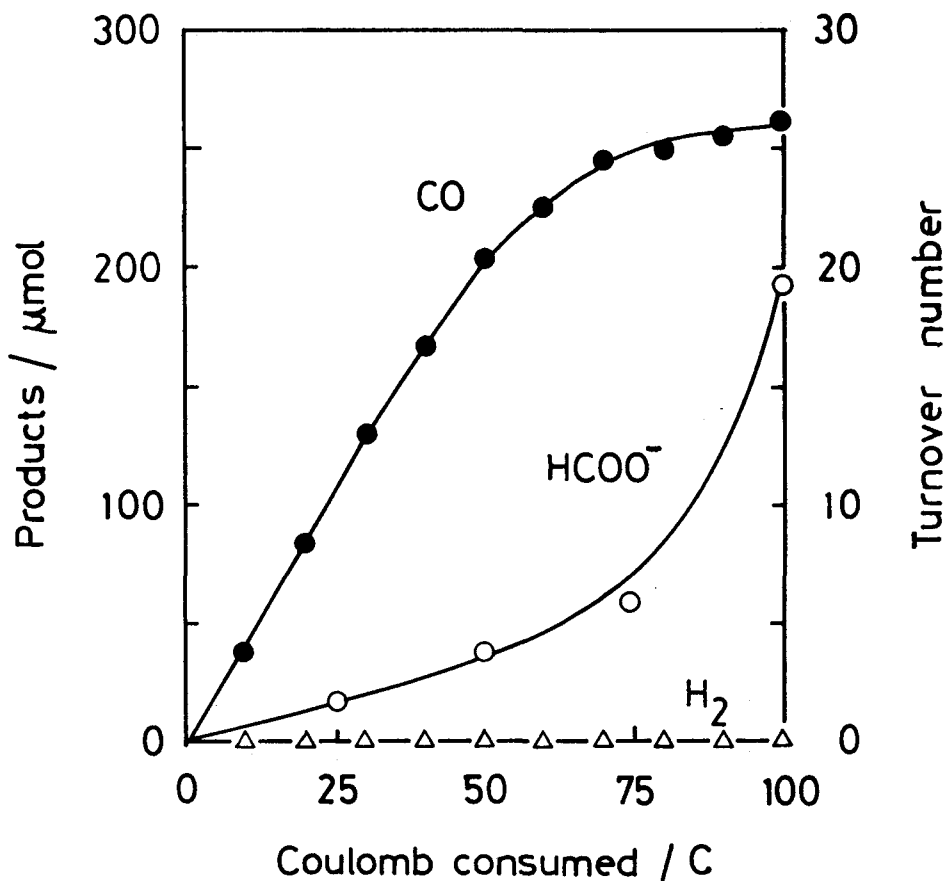


Figure 2-3. Plots of the amounts of products vs. the coulomb number consumed in the electrolysis (-1.50 V vs. SCE) of CO<sub>2</sub>-saturated H<sub>2</sub>O/DMF (1:1 v/v) solution containing [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>-</sup>(PF<sub>6</sub>)<sub>2</sub> (5.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>) and LiCl (0.10 mol dm<sup>-3</sup>) as a supporting electrolyte at 30°C.

for the formation of CO and  $\text{HCOO}^-$  based on  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  are 26.2 and 18.2, respectively, when the reduction consumed 100 coulombs, as summarized in entry 1 in Table 2-I. A similar result was obtained also in the reduction of  $\text{CO}_2$  by  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  under the same electrolysis conditions (entry 6 in Table 2-I). An increase and a decrease of the rates for the formation of  $\text{HCOO}^-$  and CO, respectively, with a lapse of time may be associated with a decrease of the proton concentration due to the consumption of protons with the progress of the reactions shown by eqs. 2-2 and 2-3. In accordance with this, the electrolysis of a  $\text{CO}_2$ -saturated  $\text{H}_2\text{O}$  (pH 6.0 buffered with  $\text{H}_3\text{PO}_4\text{-NaOH}$ )/DMF mixture (9:1 v/v) containing  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  produces only CO and  $\text{H}_2$ , both of which increase in the amount linearly with time, as shown in Figure 2-4a; no  $\text{HCOO}^-$  has been detected in solution even after the reduction consumed 100 coulombs (entry 2 in Table 2-I). This is the case with  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  used as a catalyst, as shown in Figure 2-4b. Similar results were obtained also in the reduction of  $\text{CO}_2$  in  $\text{CO}_2$ -saturated water at pH 6.0 and in a  $\text{CO}_2$ -saturated  $\text{H}_2\text{O}$  (pH 6.0)/DMF (1:1 v/v) mixture (entries 3 and 4, respectively, in Table 2-I). It is worthwhile to note that the amount of  $\text{H}_2$  evolved in the reduction of  $\text{CO}_2$  conducted in water at pH 6.0 is much larger than in  $\text{H}_2\text{O}$  (pH 6.0)/DMF (1:1 v/v) (compare entries 3 with 4 in Table 2-I). This is suggestive of the competitive reductions of  $\text{CO}_2$  and protons taking place. In fact, the amounts of CO and  $\text{H}_2$  formed increase and decrease, respectively, with the decreasing  $\text{H}_2\text{O}$  (pH 6.0)/DMF ratios

**Table 2-I.** Electrochemical CO<sub>2</sub> Reductions Catalyzed by Ruthenium Bipyridyl Complexes in H<sub>2</sub>O/DMF Systems

Entry	Catalyst <sup>a</sup>	H <sub>2</sub> O/DMF v/v	(pH) <sup>b</sup>	Coulomb consumed	Product <sup>c</sup>		
					CO	H <sub>2</sub>	HCOO <sup>-</sup>
1	[Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	1/1	Not fixed <sup>d</sup>	100	262	2	182
2		9/1	(6.0)	100	142	182	—
3		1/0	(6.0)	100	88	282	—
4		1/1	(6.0)	100	217	18	—
5		9/1	(9.5)	100	136	192	199
6	[Ru(bpy) <sub>2</sub> (CO)Cl] <sup>+</sup>	1/1	Not fixed <sup>d</sup>	90	255	21	78
7		9/1	(6.0)	100	107	217	—
8		9/1	(9.5)	75	110	170	101

<sup>a</sup> PF<sub>6</sub><sup>-</sup> salt, 5.0 x 10<sup>-4</sup> mol dm<sup>-3</sup>, 20 cm<sup>3</sup>.      <sup>b</sup> Buffered with H<sub>3</sub>PO<sub>4</sub>-NaOH.      <sup>c</sup> μmol.

<sup>d</sup> LiCl was used as an electrolyte.



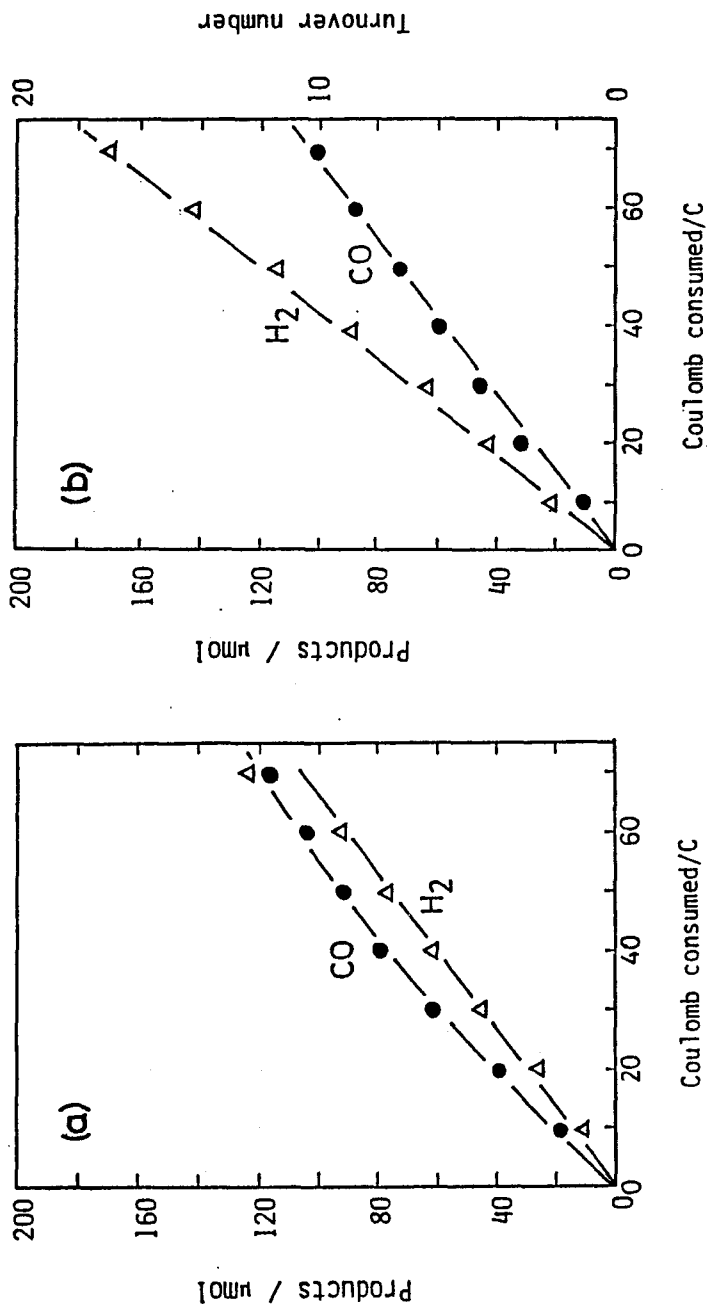
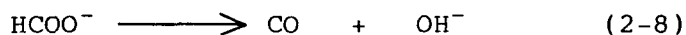


Figure 2-4. Plots of the amounts of products vs. the coulomb number consumed in the electrolysis ( $-1.50 \text{ V vs. SCE}$ ) of  $\text{CO}_2$ -saturated  $\text{H}_2\text{O}$  ( $\text{pH } 6.0$ )/DMF ( $9:1 \text{ v/v}$ ) solutions of (a)  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  and (b)  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ), buffered with  $\text{H}_3\text{PO}_4\text{-NaOH}$ .

(entries 2 - 4 in Table 2-I). It is noted that that no  $\text{HCOO}^-$  has been formed at all irrespective of the proportion of water in  $\text{H}_2\text{O}$  (pH 6.0)/DMF mixtures so long as the pH value of water is kept at 6.0 (entries 2 - 4 and 7 in Table 2-I).

The electrolysis of a  $\text{CO}_2$ -saturated alkaline solution,  $\text{H}_2\text{O}$  (pH 9.5)/DMF (9:1 v/v), of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  or  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  catalytically produces  $\text{HCOO}^-$  together with  $\text{CO}$  and  $\text{H}_2$  with no induction period, and the amounts of  $\text{HCOO}^-$  and  $\text{CO}$  increase linearly with the progress of the reaction, as shown in Figure 2-5a or 5b. It is well known that  $\text{CO}_2$  readily reacts with  $\text{OH}^-$  in alkaline solutions to afford  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , which exist as equilibrium mixtures with  $\text{CO}_2$  in solution.<sup>30</sup> The controlled potential electrolysis of an aqueous solution of  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  ( $0.10 \text{ mol dm}^{-3}$ ) in place of  $\text{CO}_2$  in the presence of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  at  $-1.50 \text{ V vs. SCE}$ , however, has produced only a stoichiometric amount of  $\text{HCOO}^-$  without evolving  $\text{CO}$  even after 50 coulombs was consumed in the reduction. Moreover, the electrolysis of an  $\text{H}_2\text{O}$  (pH 9.5)/DMF (9:1 v/v) solution of  $\text{HCOONa}$  ( $0.10 \text{ mol dm}^{-3}$ ) in the presence of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  at  $-1.50 \text{ V}$  has produced only  $\text{H}_2$ , suggesting that the conversion of  $\text{HCOO}^-$  to  $\text{CO}$  does not take place under the present electrolysis conditions (eq. 2-8). Thus, the catalytic formation of  $\text{CO}$  and  $\text{HCOO}^-$  in the



electrolysis of a  $\text{CO}_2$ -saturated  $\text{H}_2\text{O}$  (pH 9.5)/DMF (9:1 v/v)

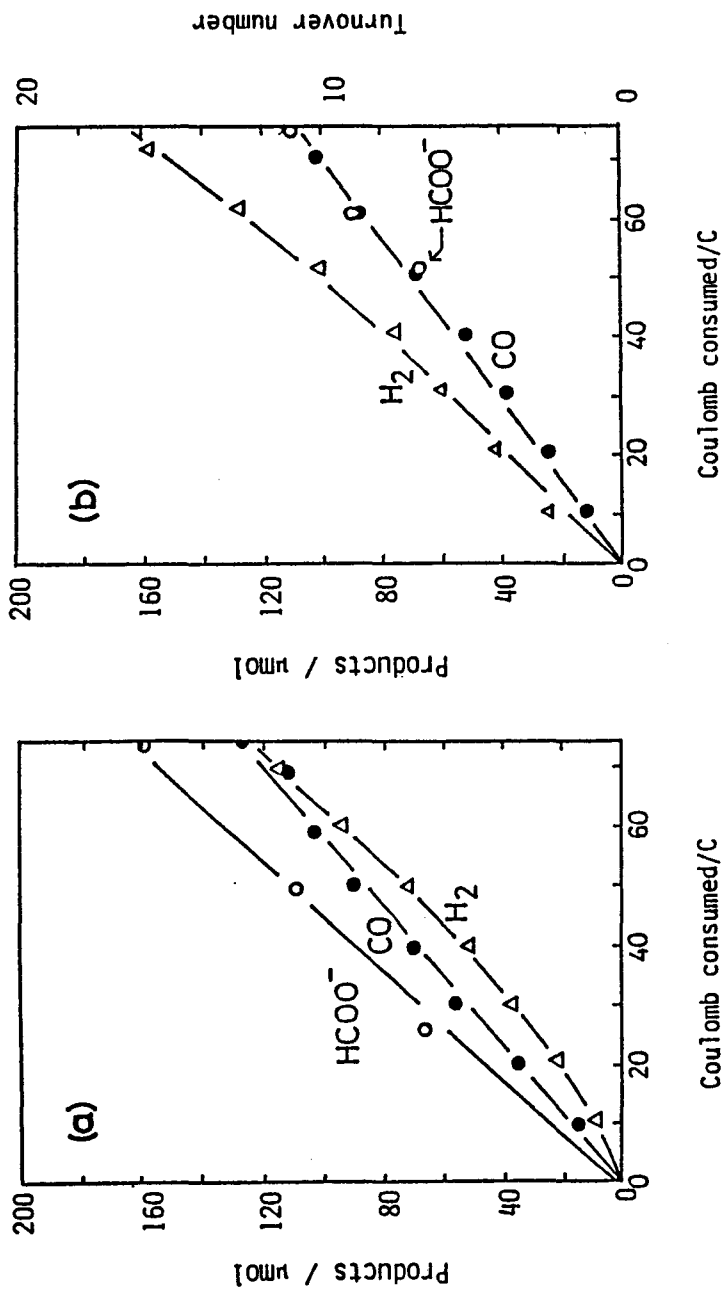


Figure 2-5. Plots of the amounts of products vs. the coulomb number consumed in the electrolysis (-1.50 V vs. SCE) of  $\text{CO}_2$ -saturated  $\text{H}_2\text{O}$  (pH 9.5)/DMF (9:1 v/v) solutions of (a)  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  and (b)  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ), buffered with  $\text{H}_3\text{PO}_4\text{-NaOH}$ .

solution either of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  or of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  (entries 5 and 8 in Table 2-I) may come from two different precursors.

#### Active Species in the Electrochemical Reduction of $\text{CO}_2$ .

In order to obtain information concerning active species in the present reaction, the spectroelectrochemical experiment was carried out with an OTTLE cell. The controlled potential electrolysis of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in  $\text{CO}_2$ -saturated DMF at  $-1.10$  V leads to the occurrence of two new bands at 350 (shoulder) and 420 nm in its electronic absorption spectrum, as shown in Figure 2-6. The spectrum obtained upon the electrolysis for 60 min agreed very closely with that of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  generated in aqueous alkaline solutions, which is consistent also with that of a DMF solution containing  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  and 2 molar equiv. of  $\text{NBu}_4^+\text{OH}^-$ .<sup>31</sup> These facts strongly suggest that the two-electron reduction product of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  reacts with  $\text{CO}_2$  to afford  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$ , which is supposed to be an important intermediate in the present electrochemical  $\text{CO}_2$  reductions.

As described in the previous section, the reduction of  $\text{CO}_2$  in  $\text{H}_2\text{O}$  (pH 9.5)/DMF (9:1 v/v) produces  $\text{HCOO}^-$  as well as CO as main products. Increasing amount of  $\text{HCOO}^-$  formed upon decreasing the proton concentration may be associated with the shift of an equilibrium among  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ , and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  in solutions (eq. 2-9 and 2-10). The equilibrium constants,  $K_1 = 1.32 \times 10^5 \text{ mol}^{-1} \text{ dm}^3$  and  $K_2 = 2.27 \times$

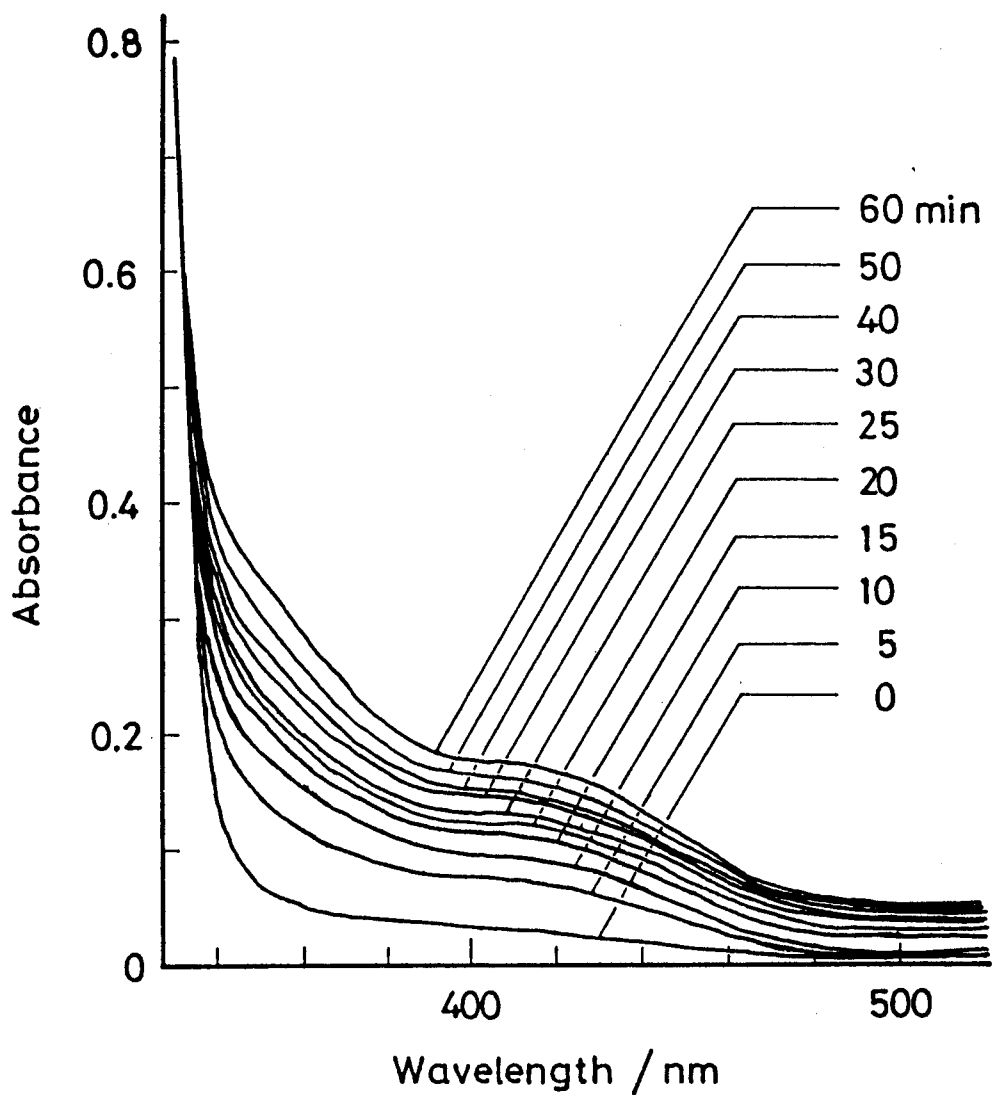
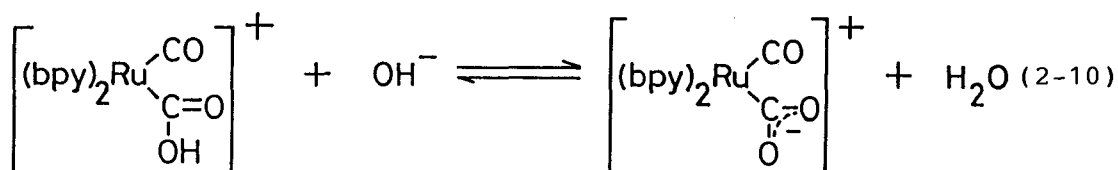
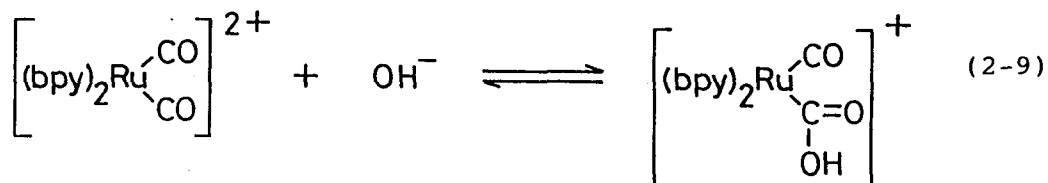


Figure 2-6. Electronic absorption spectra of a  $\text{CO}_2$ -saturated DMF solution of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) under the controlled potential electrolysis at  $-1.10 \text{ V vs. SCE}$ .



$10^4 \text{ mol}^{-1} \text{ dm}^3$  for eqs. 2-9 and 2-10, respectively, in water at  $25^\circ\text{C}$ , have little changed from those in an  $\text{H}_2\text{O}$  (at various pH)/DMF (9:1 v/v) mixture, as confirmed from the comparison of the electronic absorption spectra of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in both solvents. The distribution curves of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ , and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  calculated from the equilibrium constants  $K_1$  and  $K_2$  in  $\text{H}_2\text{O}$  are depicted in Figure 2-7, which indicates that only  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  exists as a stable species under acidic conditions. Therefore,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  may be a precursor for the production of CO in the reduction of  $\text{CO}_2$  conducted in  $\text{H}_2\text{O}$  (pH 6.0)/DMF (9:1 v/v).

In weak alkaline solutions, however,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ , and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  coexist as an equilibrium mixture; for instance the proportion of these three ruthenium species in  $\text{H}_2\text{O}$  at pH 9.5 are 12.5 : 51.0 : 36.5. The electrolysis of a weak alkaline solution, such as an  $\text{H}_2\text{O}$  (pH

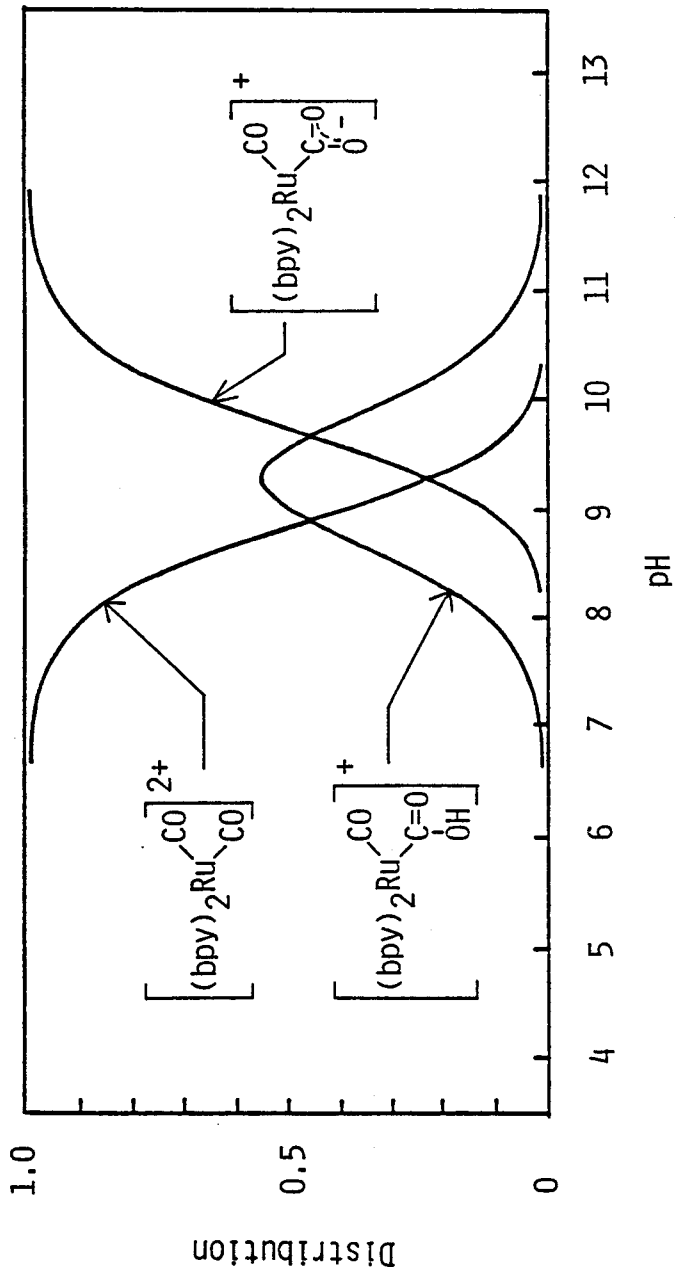


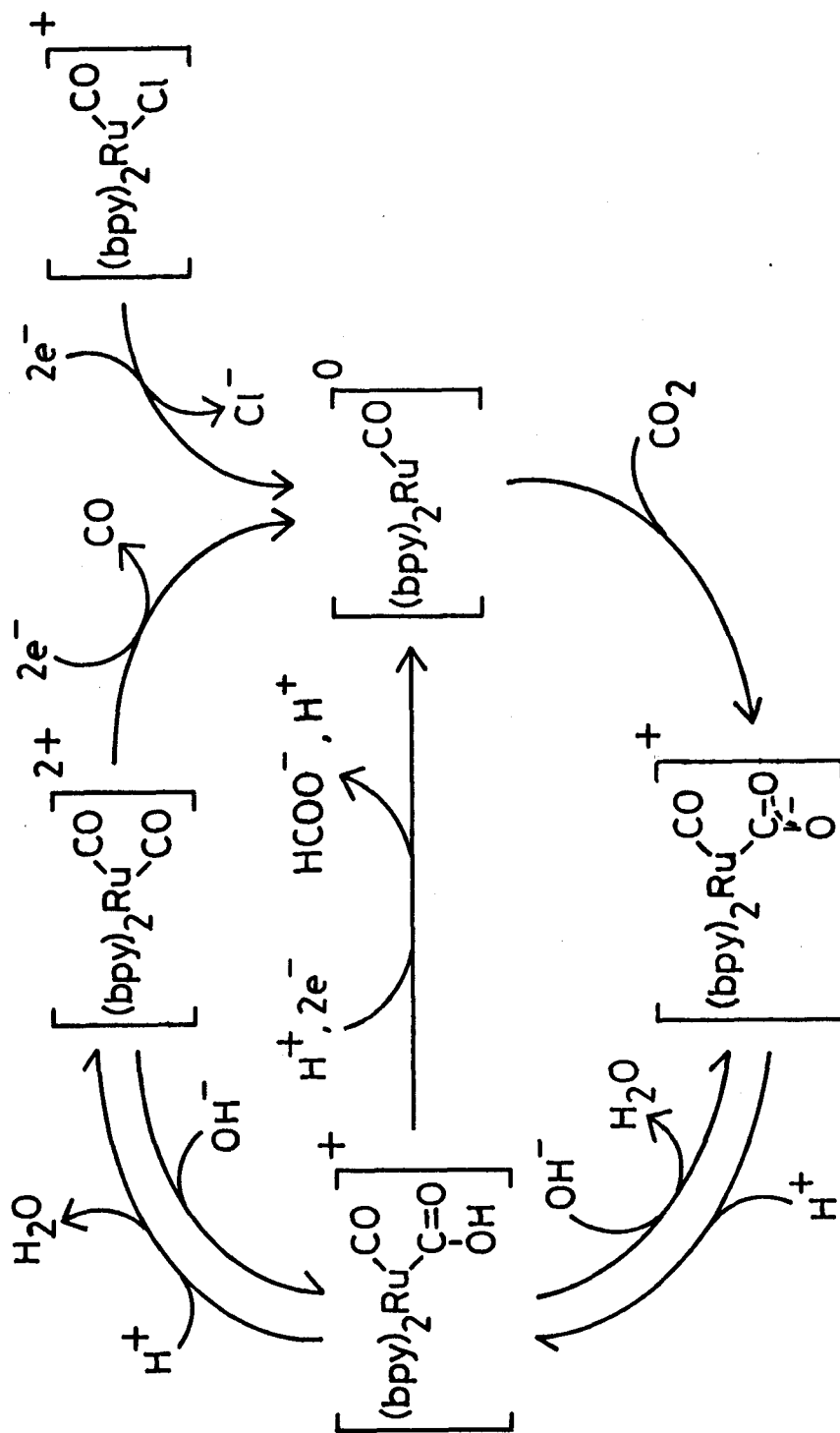
Figure 2-7. Distribution of the ruthenium species in H<sub>2</sub>O at various pH at 25°C.

9.5)/DMF (9:1 v/v) mixture, saturated with CO<sub>2</sub> produces an almost equivalent amount of HCOO<sup>-</sup> and CO. This is suggestive of [Ru(bpy)<sub>2</sub>(CO)C(O)OH]<sup>+</sup> or [Ru(bpy)<sub>2</sub>(CO)(COO<sup>-</sup>)]<sup>+</sup> being a precursor for the formation of HCOO<sup>-</sup>. This is consistent with the result that the electrolysis of an aqueous solution of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> at -1.50 V has produced a stoichiometric amount of HCOO<sup>-</sup> at pH 11.0 (buffered with Na<sub>2</sub>CO<sub>3</sub>), where [Ru(bpy)<sub>2</sub>(CO)(COO<sup>-</sup>)]<sup>+</sup> and a small amount of [Ru(bpy)<sub>2</sub>(CO)C(O)OH]<sup>+</sup> coexist. For further clarification of the precursor for the formation of HCOO<sup>-</sup> in the reduction of CO<sub>2</sub>, the reduction potentials of [Ru(bpy)<sub>2</sub>(CO)C(O)OH]<sup>+</sup> and [Ru(bpy)<sub>2</sub>(CO)(COO<sup>-</sup>)]<sup>+</sup> were examined. The cyclic voltammogram of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in H<sub>2</sub>O at pH 10.5, where [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> is almost completely converted to [Ru(bpy)<sub>2</sub>(CO)C(O)OH]<sup>+</sup> and [Ru(bpy)<sub>2</sub>(CO)(COO<sup>-</sup>)]<sup>+</sup> (Figure 2-7), showed an irreversible cathodic wave at -1.50 V vs. SCE. The peak potential of the cathodic wave was shifted by -30 mV/pH with increasing the pH value, suggesting that the reduction involves two electrons together with one proton; the proton may participate into the diffusion controlled equilibrium reaction between [Ru(bpy)<sub>2</sub>(CO)C(O)OH]<sup>+</sup> and [Ru(bpy)<sub>2</sub>(CO)(COO<sup>-</sup>)]<sup>+</sup> (eq. 2-10),<sup>22</sup> either of which undergoes a two-electron reduction to produce HCOO<sup>-</sup>.

**Mechanisms of the Reduction of CO<sub>2</sub>.** A most plausible mechanism of the reduction of CO<sub>2</sub> in this system is presented in Scheme 2-I. [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> undergoes an irreversible two-electron reduction at -0.95 V vs. SCE to give [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>0</sup>



Scheme 2-I



with 20 electrons, which may liberate CO, generating penta-coordinated  $[\text{Ru}(\text{bpy})_2(\text{CO})]{}^0$  with 18 electrons, though unstable. In the absence of  $\text{CO}_2$  in solutions,  $[\text{Ru}(\text{bpy})_2(\text{CO})]{}^0$  thus formed may be oxidized by a proton to afford  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{H}]{}^+$ ,<sup>32</sup> which reacts with another proton to evolve  $\text{H}_2$ .<sup>33</sup> In the presence of a large excess of  $\text{CO}_2$ , however,  $[\text{Ru}(\text{bpy})_2(\text{CO})]{}^0$  is converted to  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]{}^+$  possibly via  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO})]{}^0$ . This is consistent with the fact that  $\text{CO}_2$  rapidly reacts with a variety of bases B, such as  $\text{OH}^-$ ,  $\text{RO}^-$ ,  $\text{R}^-$ , and  $\text{R}_n\text{NH}_{3-n}$  (R = alkyl group, n = 0 - 3), to yield the 1:1 adducts, B-COO<sup>-</sup>. Of various  $\eta^1\text{-CO}_2$  metal complexes reported so far,<sup>34-41</sup>  $[\text{W}(\text{CO})_5\text{CO}_2]{}^{2-}$  formed in the reaction of  $[\text{W}(\text{CO})_5]{}^{2-}$  with  $\text{CO}_2$  at  $-78^\circ\text{C}$  undergoes an oxide transfer reaction with another  $\text{CO}_2$  molecule to produce  $[\text{W}(\text{CO})_6]$  and  $\text{CO}_3^{2-}$  at room temperature.<sup>34</sup> Although  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]{}^+$  does not undergo such an oxide transfer reaction with another  $\text{CO}_2$  molecule, it may easily be converted to  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]{}^{2+}$  via  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]{}^+$  in acidic conditions according to the equilibrium reactions shown in eqs. 2-9 and 2-10, and in Scheme 2-I. Thus, the reduction of  $\text{CO}_2$  conducted in acidic media produces only CO. On the other hand, in weak alkaline solutions such as pH 9.5,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]{}^+$  (or  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]{}^+$ ) exists as a predominant species (Figure 2-7), which may undergo a two-electron reduction involving the participation of one proton to give  $\text{HCOO}^-$  with regenerating the penta-coordinated ruthenium(0) complex,  $[\text{Ru}(\text{bpy})_2(\text{CO})]{}^0$ . The evolution of CO at the same time may come from the two-electron reduction of

$[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  existing as a minor component (Figure 2-7) in the solution.

As described in the previous section, there is a close similarity between  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  as catalysts for the reduction of  $\text{CO}_2$ , suggesting that the two-electron reduction of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2\text{Cl}]^+$  results in the dissociation of  $\text{Cl}^-$  to afford the unstable pentacoordinated intermediate  $[\text{Ru}(\text{bpy})_2(\text{CO})]^{0}$ , which may react with  $\text{CO}_2$  to generate  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$ . Several attempts to identify the formation of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  in electrochemical two-electron reductions of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  at -1.40 to -1.50 V vs. SCE in  $\text{CO}_2$ -saturated anhydrous DMF, however, have resulted in the formation of only an insoluble black precipitate. This is probably due to instability of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  in anhydrous DMF at such potentials. It is well known that  $[\text{Ru}(\text{bpy})_2\text{XY}]^{n+}$  (X, Y = pyridine derivatives, halides, phosphines, and so on; n = 0 - 2) undergoes two successive one-electron reversible or quasi-reversible reductions,<sup>42</sup> when the added electrons may localize mainly in  $\pi^*$ -orbitals of the bipyridine ligands.<sup>43, 44</sup> A strong  $\pi$ -electron acceptor CO ligand, however, may resist such an electron localization in  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{0}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^-$ . Thus, two-electron reductions of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$  may be followed by chemical reactions possibly to generate  $[\text{Ru}(\text{bpy})_2(\text{CO})]^{0}$ . The participation of  $[\text{Ru}(\text{bpy})_2(\text{CO})]^{0}$  in the catalytic cycle of the present  $\text{CO}_2$  reduction reasonably explains the formation of CO and  $\text{HCOO}^-$  depending on pH of the solutions.

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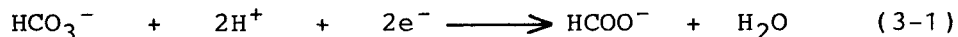


## Chapter 3

### Selective HCOO<sup>-</sup> Formation on the Electrochemical CO<sub>2</sub> Reduction

#### 3-1 Introduction

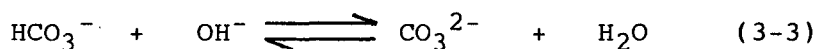
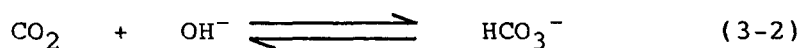
In the electrochemical CO<sub>2</sub> reductions catalyzed by transition metal complexes,<sup>1-4</sup> Ni(cyclam)<sup>1</sup> and Re(bpy)(CO)<sub>3</sub>Cl<sup>2</sup> are well known to catalyze selective CO formation. As a catalyst for the electrochemical generation of HCOO<sup>-</sup> is reported Rh(diphos)<sub>2</sub>Cl, however the maximum current efficiency is relatively low: 42.5%. Selective HCOO<sup>-</sup> formation from HCO<sub>3</sub><sup>-</sup> (eq. 3-1) is reported also



in the Pd-impregnated Pt or W electrode<sup>3</sup>; the current efficiency is high (85%), while the current density is considerably low (0.05 - 0.1 mA cm<sup>-1</sup>). Thus, selective HCOO<sup>-</sup> formation by the electrochemical CO<sub>2</sub> reduction catalyzed by transition metal complexes is hardly reported so far.

In the previous chapter, it has been described that the CO<sub>2</sub> reduction catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> (bpy = 2,2'-bipyridine) produced only CO under the controlled potential electrolysis at -1.50 V vs. SCE in a DMF/H<sub>2</sub>O (1:9 v/v) solution buffered at pH

6.0, while a mixture of CO and HCOO<sup>-</sup> (7:10) was formed at pH 9.5 under otherwise the same electrolysis conditions. Increasing the pH of aqueous solutions, however, resulted in decreasing the reactivity due to the conversion from CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> (eqs. 3-2 and 3-3), being inactive species toward the reduction



with [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>. Therefore, selective HCOO<sup>-</sup> formation has never been attained.

This chapter describes the formation of HCOO<sup>-</sup> depending on the acidity of proton sources in the electrochemical CO<sub>2</sub> reductions catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in CH<sub>3</sub>OH and CH<sub>3</sub>CN, where very efficient formation of HCOO<sup>-</sup> has been accomplished.

### 3-2 Experimental Section

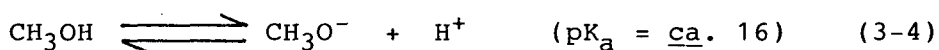
**Materials.** Methyl amine hydrochlorides are purchased or prepared by the reaction between methyl amines and hydrogen chloride, and recrystallized several times with CH<sub>3</sub>CN/diethyl ether. Commercially available guaranteed reagent grades of phenol and NBu<sup>n</sup><sub>4</sub>ClO<sub>4</sub> were used without further purification. CH<sub>3</sub>OH was distilled with Na, and CH<sub>3</sub>CN was purified by distillation five times with P<sub>2</sub>O<sub>5</sub>.

**Electrochemical CO<sub>2</sub> Reductions.** The electrolysis cell is essentially the same as described in chapter 2, except that anode and cathode compartments are separated by a nafion membrane. An Hg pool (3.1 cm<sup>2</sup>) and a platinum plate (ca. 3 cm<sup>2</sup>) were used as working and auxiliary electrodes, respectively. The reaction was conducted in CO<sub>2</sub>-saturated CH<sub>3</sub>OH or CH<sub>3</sub>CN (20 cm<sup>3</sup>) containing NBu<sup>n</sup><sub>4</sub>ClO<sub>4</sub> (0.10 mol dm<sup>-3</sup>) and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> (5.0 x 10<sup>-4</sup> mol dm<sup>-3</sup>). CO and H<sub>2</sub> were analyzed by gas chromatography and the amount of HCOO<sup>-</sup> was determined by an isotachophoretic analyzer, in which an aqueous Triton X-100 (0.2 vol%) solution containing β-alanine (0.02 mol dm<sup>-3</sup>) and HCl (0.01 mol dm<sup>-3</sup>) is used as a leading electrolyte.

### 3-3 Results and Discussion

**Electrochemical CO<sub>2</sub> Reductions in Alcohols.** In order to attain selective HCOO<sup>-</sup> formation on electrochemical CO<sub>2</sub> reductions catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>, the reaction requires proton sources excluding H<sub>2</sub>O, which is a comparatively strong acid as well as giving OH<sup>-</sup> in the course of the reaction to afford HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> as inactive species for the reduction with [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>. Therefore, the electrochemical CO<sub>2</sub> reductions were performed by using CH<sub>3</sub>OH as a proton source. Cyclic voltammograms of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in CH<sub>3</sub>OH under N<sub>2</sub> and CO<sub>2</sub> atmospheres by using a hanging mercury drop electrode (HMDE) with the

surface area  $2.22 \pm 0.07 \text{ mm}^2$  are shown in Figure 3-1. The cyclic voltammogram in an  $\text{N}_2$ -saturated  $\text{CH}_3\text{OH}$  solution shows a reduction peak at  $-1.05 \text{ V vs. SCE}$  and a shoulder peak at  $-1.45 \text{ V}$  in the irreversible cathodic wave, the latter of which may correspond to the  $\text{H}_2$  evolution. On the other hand, the cyclic voltammogram under  $\text{CO}_2$  atmosphere shows strong cathodic currents begin to flow around  $-1.0 \text{ V vs. SCE}$  with a shoulder peak at  $-1.10 \text{ V vs. SCE}$ . Removal of  $\text{CO}_2$  from  $\text{CO}_2$ -saturated  $\text{CH}_3\text{OH}$  containing  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  by bubbling  $\text{N}_2$  through the solution for 30 min resulted in complete disappearance of the strong cathodic current to give the cyclic voltammogram in  $\text{N}_2$ -saturated  $\text{CH}_3\text{OH}$ . Therefore, the cyclic voltammograms exhibit that  $\text{CH}_3\text{OH}$  functions efficiently as a proton source ( $\text{pK}_a = \text{ca. } 16$ ,<sup>5</sup> eq. 3-4) for the electrochemical



$\text{CO}_2$  reduction catalyzed by  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ .

The result of the controlled potential electrolysis of a  $\text{CO}_2$ -saturated  $\text{CH}_3\text{OH}$  solution containing  $\text{NBu}_4^+\text{ClO}_4^-$  ( $0.10 \text{ mol dm}^{-3}$ ) as a supporting electrolyte and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) as a catalyst at  $-1.50 \text{ V vs. SCE}$  is depicted in Figure 3-2a, which shows  $\text{HCOO}^-$ ,  $\text{CO}$  and  $\text{H}_2$  being produced catalytically and the amounts increasing almost linearly against coulombs consumed. The main product is  $\text{HCOO}^-$  whose amount of  $254 \mu\text{mol}$  at 100 coulombs, and the current efficiency was 49%.  $\text{CO}$  and  $\text{H}_2$  also were formed with current efficiencies of 32 and 5%, respectively.

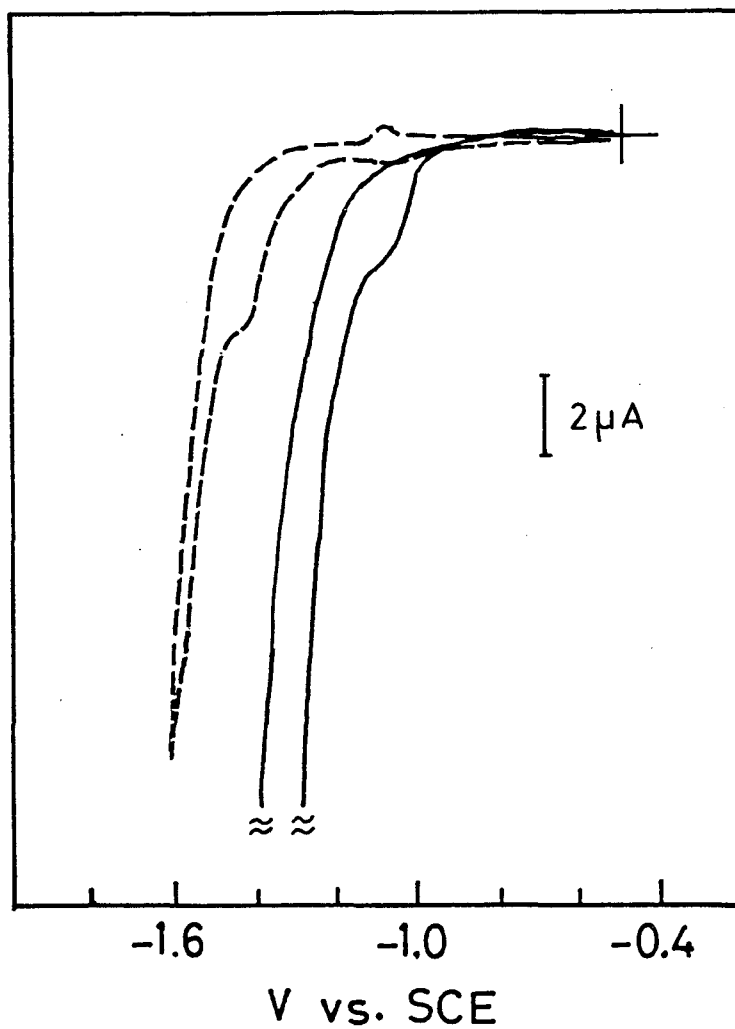


Figure 3-1. Cyclic voltammograms of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) in  $\text{CH}_3\text{OH}$  containing  $\text{NBu}_4^+\text{ClO}_4^-$  ( $0.10 \text{ mol dm}^{-3}$ ) as a supporting electrolyte under  $\text{N}_2$  (---) and  $\text{CO}_2$  (—) atmospheres, using an Hg electrode (sweep rate =  $0.10 \text{ V s}^{-1}$ ).

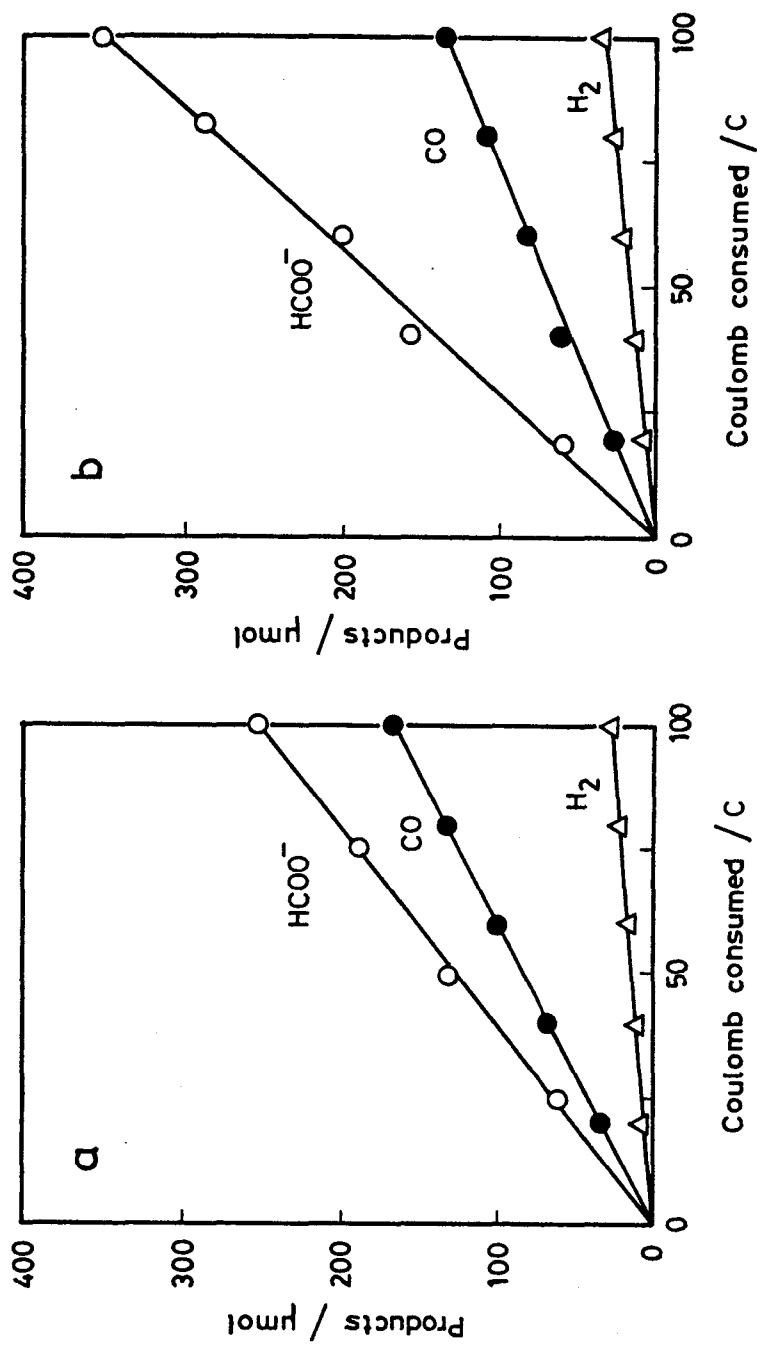
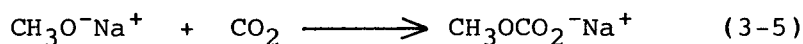


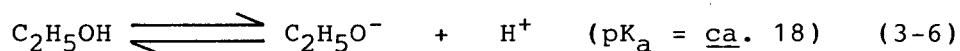
Figure 3-2. Electrochemical CO<sub>2</sub> reduction catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in CH<sub>3</sub>OH (a) and in CH<sub>3</sub>OH containing CH<sub>3</sub>ONa (0.10 mol dm<sup>-3</sup>) (b); -1.50 V vs. SCE, NBu<sub>4</sub><sup>+</sup>ClO<sub>4</sub><sup>-</sup> (0.10 mol dm<sup>-3</sup>).

Therefore, it is proved that CH<sub>3</sub>OH can act as a proton donor. In order to perform more selective HCOO<sup>-</sup> formation for the present CO<sub>2</sub> reduction, the electrolysis was conducted in CO<sub>2</sub>-saturated CH<sub>3</sub>OH containing sodium methoxide, CH<sub>3</sub>O<sup>-</sup>Na<sup>+</sup> (0.1 mol dm<sup>-3</sup>) as an electrolyte at -1.50 V vs. SCE. The result is shown in Figure 3-2b, which reveals that HCOO<sup>-</sup>, CO, and H<sub>2</sub> are produced almost linearly against coulombs consumed with current efficiencies of 68, 26, and 6%, respectively. The reaction in CH<sub>3</sub>OH under alkaline conditions also increased the amount of HCOO<sup>-</sup>, and decreased that of CO, however highly selective HCOO<sup>-</sup> formation has never been achieved. The reaction has not been conducted under further alkaline conditions since the reaction of CH<sub>3</sub>O<sup>-</sup>Na<sup>+</sup> with CO<sub>2</sub> occurred to produce CH<sub>3</sub>OCO<sub>2</sub><sup>-</sup>Na<sup>+</sup> (eq. 3-5), which



is inactive species for the present CO<sub>2</sub> reduction.

Ethanol as a less donative proton source was examined for the reduction of CO<sub>2</sub> under the controlled potential electrolysis conditions. However, the reaction has scarcely proceeded; the amounts of HCOO<sup>-</sup> and CO produced were very small. Thus, the pK<sub>a</sub> of ethanol (ca. 18<sup>5</sup>; eq. 3-6) may be too large to function as the



proton source in the present electrochemical CO<sub>2</sub> reduction.

Therefore, no highly selective  $\text{HCOO}^-$  formation has been achieved in alcohol though the selectivity of  $\text{HCOO}^-$  generation was largely improved as compared with that in DMF/water.

**Electrochemical  $\text{CO}_2$  Reductions in  $\text{CH}_3\text{CN}$  in the presence of organic acids.** The controlled potential electrolysis was conducted in a  $\text{CO}_2$ -saturated  $\text{CH}_3\text{CN}$  solution containing organic acids as proton sources. The results are summarized in Table 3-I, which confirms that the relative amounts of reduction products,  $\text{HCOO}^-$ ,  $\text{CO}$ , and  $\text{H}_2$  are largely dependent on the  $\text{pK}_a$  value of proton sources; the amount of  $\text{HCOO}^-$  increases with increasing the  $\text{pK}_a$  value, and the current efficiency ( $\eta$ ) for its formation reaches 84.3% in the presence of  $(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$  as a proton source. This is because no conversion from the intermediate,  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  to  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  may occur for low acidity of  $(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$ . On the other hand, the amounts of  $\text{H}_2$  evolution increases with decreasing the  $\text{pK}_a$  value. In the case of benzoic acid used as a proton source, the current efficiency for  $\text{H}_2$  evolution attains 50.7%, suggesting that the attack of  $\text{CO}_2$  and  $\text{H}_2$  to the active site of the catalyst occurs competitively.

The present electrochemical  $\text{CO}_2$  reduction reveals not only high selectivity of the  $\text{HCOO}^-$  formation but also high current density in the reduction of  $\text{CO}_2$ , the latter of which corresponds to large reaction velocity. The largest  $\eta(\text{HCOO}^-)$  value reported so far in the reduction of  $\text{HCO}_3^-$  is ca. 85% upon using a viologen



**Table 3-I.** The electrochemical CO<sub>2</sub> reduction catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in the presence of several proton sources in CH<sub>3</sub>CN<sup>a)</sup>

Proton source <sup>b)</sup>	pK <sub>a</sub> <sup>c)</sup> in CH <sub>3</sub> CN	Product <sup>d)</sup> / μmol			Current density <sup>e)</sup> mA cm <sup>-2</sup>	
		HCOO <sup>-</sup>	CO	H <sub>2</sub>		
(CH <sub>3</sub> )NH <sub>2</sub> ·HCl	15.6	332 (64.1)	103 (19.9)	17 (3.3)		1.6
(CH <sub>3</sub> ) <sub>2</sub> NH·HCl	15.8	437 (84.3)	13 (2.4)	35 (6.8)		3.3
(CH <sub>3</sub> ) <sub>3</sub> N·HCl	14.8	288 (55.5)	32 (6.1)	158 (30.5)		3.3
C <sub>6</sub> H <sub>5</sub> COOH	12.0	117 (22.5)	51 (9.9)	263 (50.7)		2.2
C <sub>6</sub> H <sub>5</sub> OH	f)	420 (81.0)	84 (16.3)	2 (0.3)		2.3

a) -1.30 V vs. SCE. b) 0.20 mol dm<sup>-3</sup>. c) Charlot, G.; Tretmillon, B. "Chemical Reactions in Solvents and Melts"; Pergamon Press, New York, 1969. d) The current efficiency (%) for the formation of the product after the consumption of 100 C in parenthesis. e) Average value for 100 C. f) No available datum in literatures.

polymer coated Pd electrode, however the current density in the reaction was very low ( $0.05 - 0.1 \text{ mA cm}^{-2}$ ).<sup>3</sup> In view of large current densities of the present reactions ( $1.6 - 3.3 \text{ mA cm}^{-2}$ , Table 3-I), the electrochemical  $\text{CO}_2$  reduction described here is not only most selective for the  $\text{HCOO}^-$  formation but also fastest in the rate of reduction.

### 3-4 References

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## Chapter 4

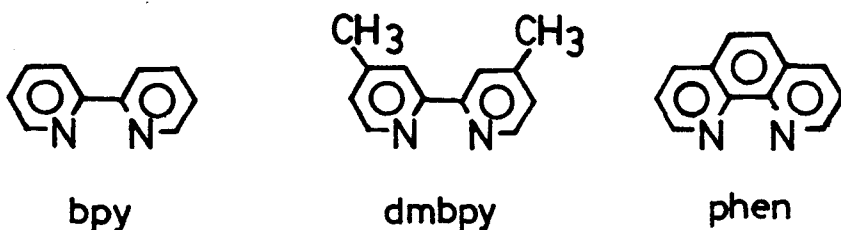
### Ligand Effect of the Ruthenium Complexes on Electrochemical CO<sub>2</sub> Reduction

#### 4-1 Introduction

Products obtained in the electrochemical CO<sub>2</sub> reductions may depend on the nature not only of central metal ions but also of ligands of transition metal catalysts. For instance, Ni and Co complexes with macrocycles,<sup>1</sup> Pd-phosphine complexes,<sup>2</sup> and pyridine complexes of Re,<sup>3</sup> Ru<sup>4</sup> and Rh<sup>5</sup> are known as catalysts to generate CO in the electrochemical CO<sub>2</sub> reductions. On the other hand, as the catalysts for HCOO<sup>-</sup> formation are reported Rh-phosphine complexes,<sup>6</sup> phthalocyanine complexes and macrocycles of Co and Ni,<sup>7</sup> Pd-based electrode,<sup>8</sup> Ru-bipyridine complexes,<sup>9</sup> and iron-sulfur clusters.<sup>10</sup> As other products in the CO<sub>2</sub> reduction are reported HCHO,<sup>11</sup> CH<sub>3</sub>OH,<sup>12</sup> and CH<sub>4</sub>,<sup>13</sup> all of which are those produced by solid metal catalysts except for the reduction of CO<sub>2</sub> with K<sub>2</sub>Fe[Fe(CN)<sub>6</sub>] to afford CH<sub>3</sub>OH.<sup>12a</sup> Thus, the electrochemical reduction of CO<sub>2</sub> can be controlled by changing the metal ion and/or the ligand of transition metal catalysts. While a variety of metal ions have been examined as transition metal complex catalysts for the electrochemical CO<sub>2</sub> reduction, there are only a few reports concerning on the effect of ligands on the catalytic

activity of transition metal complexes.<sup>14</sup>

This chapter describes the electrochemical CO<sub>2</sub> reductions catalyzed by ruthenium complexes of bipyridine derivatives, 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), and 1,10-phenanthroline (phen). Electrochemical properties of those ruthenium complexes and the equilibrium reaction between the ruthenium complexes and OH<sup>-</sup> also are discussed.



#### 4-2 Experimental Section

**Material.** NBu<sub>4</sub><sup>n</sup>OH was purchased as a 10% methanol solution, and used without further purification.

**Preparation of [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub>.** A 90%-HCOOH solution (50 cm<sup>3</sup>) containing RuCl<sub>3</sub>·nH<sub>2</sub>O (1.0 g, 3.8 mmol), which is commercially available, was refluxed under N<sub>2</sub> in the dark for 3 h, during which time color of the solution turned to orange from dark blue. Then, the solution was allowed to stand at room temperature, followed by evaporation to dryness in vacuo. Thus a polymeric ruthenium complex [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> was obtained as an orange solid. Anal. Calcd for RuC<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>: C, 10.5, H, 0.0%.

Found: C, 11.7, H, 0.6%.

**Preparation of Ru(bpy)(CO)<sub>2</sub>Cl<sub>2</sub>.** An ethanol/water (1:1 v/v; 38 cm<sup>3</sup>) solution containing [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> (0.5 g, 2.2 mmol) and 2,2'-bipyridine (0.3 g, 1.9 mmol) was refluxed at 70 - 80°C for one hour under N<sub>2</sub>. After refluxed, a yellow crystal precipitated was collected by filtration and recrystallized from acetonitrile; 68% yield, mp > 300°C. Anal. Calcd for RuC<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>: C, 37.60, H, 2.09, N, 7.31%. Found: C, 37.42, H, 2.27, N, 7.26%.

**Preparation of Ru(dmbpy)(CO)<sub>2</sub>Cl<sub>2</sub>.** Ru(dmbpy)(CO)<sub>2</sub>Cl<sub>2</sub> was prepared by the method similar to Ru(bpy)(CO)<sub>2</sub>Cl<sub>2</sub> by using 4,4'-dimethyl-2,2'-bipyridine in place of 2,2'-bipyridine; 23% yield. Anal. Calcd for RuC<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>: C, 40.79, H, 2.93, N, 6.80%. Found: C, 41.19, H, 3.10, N, 7.06%.

**Preparation of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.** Being different from the method described in Chapter 1, where the yield was very low; [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was prepared as follow; an ethanol/water (5:4 v/v; 180 cm<sup>3</sup>) solution containing [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> (2.0 g, 8.8 mmol) and 2,2'-bipyridine (5.0 g, 32 mmol) was refluxed under N<sub>2</sub> for 4 h. The solution was cooled, followed by the addition of NH<sub>4</sub>PF<sub>6</sub> dissolved in a small amount of water to afford a white precipitate, which was recrystallized twice with acetone/ether; 10% yield. Anal. Calcd for RuC<sub>22</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>F<sub>16</sub>: C, 34.80, H, 2.12, N, 7.38%. Found: C, 35.01, H, 2.15, N, 7.40%.

**Preparation of  $[\text{Ru}(\text{bpy})(\text{dmbpy})(\text{CO})_2](\text{PF}_6)_2 \cdot 0.5(\text{CH}_3)_2\text{CO}$ .**

An ethanol/water (10:7 v/v; 170 cm<sup>3</sup>) solution containing Ru-(dmbpy)(CO)<sub>2</sub>Cl<sub>2</sub> (0.41 g, 1.0 mmol) and 2,2'-bipyridine (0.18 g, 1.2 mmol) was refluxed under N<sub>2</sub> for 24 h. After cooled to room temperature, ethanol in the solution was evaporated to a half volume in vacuo, and the resulting precipitates of unreacted Ru(dmbpy)(CO)<sub>2</sub>Cl<sub>2</sub> and 2,2'-bipyridine were filtered. To the filtrate was added an aqueous NH<sub>4</sub>PF<sub>6</sub> solution to give a precipitate, which was recrystallized twice with acetone/ether, giving yellow crystals; 53% yield;  $\nu(\text{C}\equiv\text{O})$  2024, 2076 cm<sup>-1</sup>. Anal. Calcd for RuC<sub>25.5</sub>H<sub>23</sub>N<sub>4</sub>O<sub>2.5</sub>P<sub>2</sub>F<sub>12</sub>: C, 37.60, H, 2.76, N, 6.95%. Found: C, 37.52, H, 2.84, N, 6.86%.

**Preparation of  $[\text{Ru}(\text{dmbpy})_2(\text{CO})_2](\text{PF}_6)_2$ .**  $[\text{Ru}(\text{dmbpy})_2-$

(CO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was prepared by the method similar to  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$ , using 4,4'-dimethyl-2,2'-bipyridine in place of 2,2'-bipyridine; 12% yield;  $\nu(\text{C}\equiv\text{O})$  2024, 2080 cm<sup>-1</sup>. Anal. Calcd for RuC<sub>26</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>: C, 38.28, H, 2.94, N, 6.87%. Found: C, 38.21, H, 3.04, N, 6.77%.

**Preparation of  $[\text{Ru}(\text{phen})_2(\text{CO})_2](\text{PF}_6)_2$ .**

An aqueous 90% formic acid solution (50 cm<sup>3</sup>) of RuCl<sub>3</sub>·nH<sub>2</sub>O (1.0 g) was refluxed under N<sub>2</sub> for 5 h. The resulting clear orange solution was allowed to stand at room temperature, and evaporated to dryness under reduced pressure to afford an orange solid, which was

dissolved in H<sub>2</sub>O/ethanol (1:4 v/v) containing 1,10-phenanthroline (1.0 g, 5.5 mmol). Then, the solution was refluxed under N<sub>2</sub> for 2 h, followed by cooling to 0°C to give an orange precipitate of Ru(phen)(CO)<sub>2</sub>Cl<sub>2</sub>. The crude product thus obtained and 1,10-phenanthroline (1.0 g, 5.5 mmol) was dissolved in H<sub>2</sub>O/ethanol (2:1 v/v, 100 cm<sup>3</sup>), and heated under refluxing conditions for 24 h. To the solution was added a concentrated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> at room temperature to yield an off-white precipitate, which was purified by recrystallization from acetone/ether; 78% yield. Anal. Calcd for C<sub>26</sub>H<sub>16</sub>F<sub>12</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Ru: C, 38.65; H, 2.00; N, 6.93%. Found: C, 38.73; H, 2.13; N, 7.08%.

**Preparation of [Ru(phen)<sub>2</sub>(CO)Cl](PF<sub>6</sub>).** A DMF solution (20 cm<sup>3</sup>) containing RuCl<sub>3</sub>·nH<sub>2</sub>O (1.0 g, 3.8 mmol), 1,10-phenanthroline (1.4 g, 7.7 mmol), and LiCl (1.5 g, 0.35 mmol) was refluxed under N<sub>2</sub> for 8 h. After cooled to room temperature, the solution was mixed with acetone (100 cm<sup>3</sup>) and the mixture was allowed to stand overnight at 0°C to give a precipitate of Ru(phen)<sub>2</sub>Cl<sub>2</sub>, which was collected by filtration, washed with ether and then water, and dried in vacuo. Ru(phen)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (1.0 g, 1.8 mmol) thus obtained was dissolved in 90%-HCOOH (30 cm<sup>3</sup>) and the solution was refluxed under N<sub>2</sub> for 6 h. After cooled to room temperature, the solution was evaporated to dryness. The resulting residue was dissolved in H<sub>2</sub>O, followed by the addition of an aqueous NH<sub>4</sub>PF<sub>6</sub> solution to afford a solid, which was collected by filtration and recrystallized from acetone/ether.



Anal. Calcd for  $\text{RuC}_{25}\text{H}_{16}\text{N}_4\text{OClPF}_6$ : C, 44.82, H, 2.41, N, 8.36%.

Found: C, 44.38, H, 2.75, N, 8.02%.

#### 4-3 Results and Discussion

Equilibrium reactions among  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$ ,  $[\text{RuL}_1\text{L}_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ , and  $[\text{RuL}_1\text{L}_2(\text{CO})(\text{COO}^-)]^+$ . The electronic absorption spectra of  $[\text{Ru}(\text{bpy})(\text{dmbpy})(\text{CO})_2]^{2+}$  in an aqueous solution (pH 5.31) and upon the addition of an aqueous KOH solution to the original weak acidic solution are shown in Figure 4-1, which reveals that the bands at 251, 301 and 311 nm observed in the acidic medium are weakened with increasing the pH value, and new bands at 277, 343 and 422 nm are strengthened with isosbestic points at 259, 296 and 322 nm. Similar spectra are observed for an aqueous  $[\text{Ru}(\text{dmbpy})_2(\text{CO})_2]^{2+}$  solution; upon increasing the pH value, the absorption bands at 248, 301 and 313 nm disappeared and the bands at 268, 342 and 428 nm newly appeared with isosbestic points at 256, 296 and 322 nm, as shown in Figure 4-2. Spectral changes of the both complexes are essentially consistent with that of the corresponding bis(2,2'-bipyridine) complex,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ; in alkaline media one of the carbonyl groups of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  may be attacked by  $\text{OH}^-$  to give  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ , which undergoes the deprotonation reaction to afford  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$ . The equilibrium constants between  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$  and  $[\text{RuL}_1\text{L}_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$  ( $K_1$ ), and between the latter and  $[\text{RuL}_1\text{L}_2(\text{CO})(\text{COO}^-)]^+$  ( $K_2$ ) evaluated

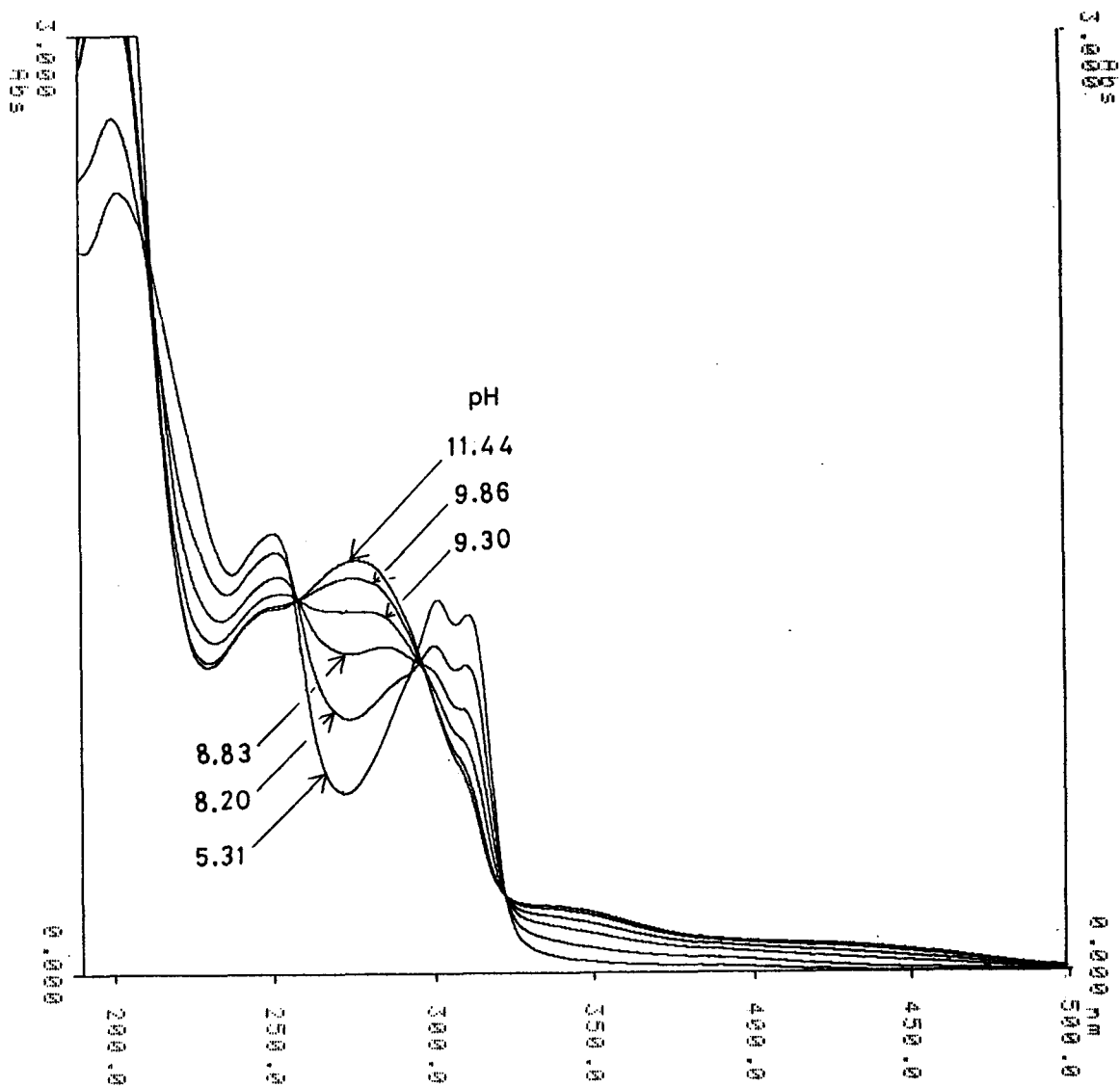


Figure 4-1. Electronic absorption spectra of  $[\text{Ru}(\text{bpy})(\text{dmbpy})-(\text{CO})_2]^{2+}$  ( $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ) in  $\text{H}_2\text{O}$  at various pH (25°C).

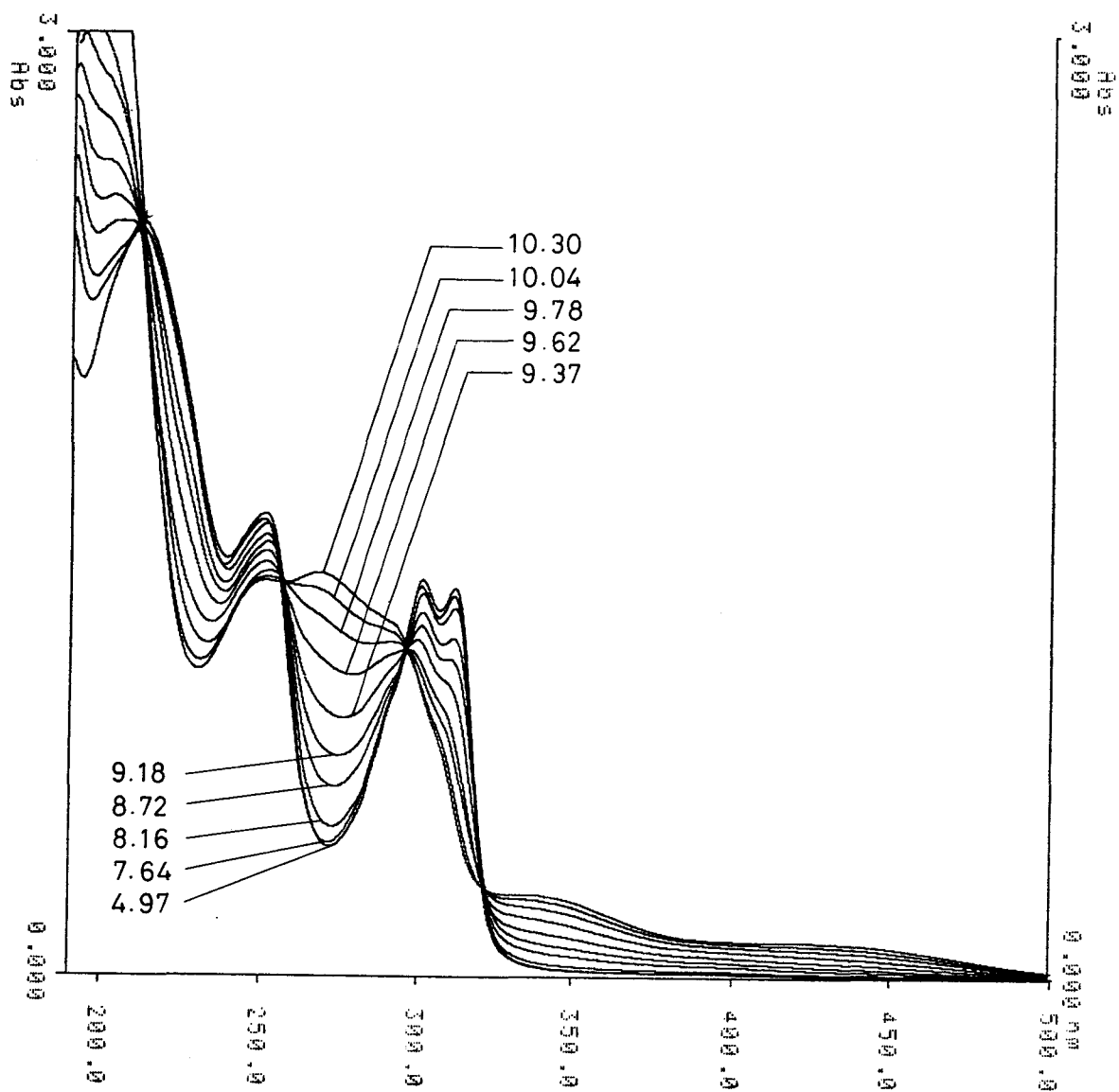


Figure 4-2. Electronic absorption spectra of  $[\text{Ru}(\text{dmbpy})_2(\text{CO})_2]^{2+}$  ( $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ) in  $\text{H}_2\text{O}$  at various pH ( $25^\circ\text{C}$ ).

from titration curves are listed in Table 4-I. Both the equilibrium constants become small with introducing 4,4'-dimethyl-2,2'-bipyridine with an electron donating CH<sub>3</sub> group as a ligand in place of 2,2'-bipyridine.

**Electrochemical properties of ruthenium species.** The cyclic voltammograms of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in CH<sub>3</sub>CN under N<sub>2</sub> and CO<sub>2</sub> atmospheres are shown in Figure 4-3a; there are observed an irreversible cathode peak around -1.03 V vs. SCE and some anode peaks in the range -1.0 to +1.5 V vs. SCE under N<sub>2</sub> atmosphere, of which the peak around -0.5 V vs. SCE is strong. Those anodic currents may correspond to oxidation of the reduction products of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>, because no anode peak is observed when the scanning was conducted in the range 0 V to +1.5 V vs. SCE (a dotted line in Figure 4-3a). The cathode peak of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> at -1.03 V vs. SCE is shifted to negative potentials upon introduction of a dmbpy ligand in place of bpy and the potentials exhibited by [RuL<sub>1</sub>L<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> (L<sub>1</sub>L<sub>2</sub> = (bpy)<sub>2</sub>, (bpy)(dmbpy), (dmbpy)<sub>2</sub>, (phen)<sub>2</sub>) in CH<sub>3</sub>CN are more negative than those in DMF, as listed in Table 4-II. The cyclic voltammogram in the presence of low concentrations of CO<sub>2</sub> gives a large cathode current around -1.7 V vs. SCE as well as two shoulders at ca. 1.4 and -1.6 V vs. SCE. The anode peak at -0.5 V vs. SCE disappeared and the new oxidation peaks around -1.5 V, -1.3 V and -1.0 V vs. SCE generated.

On the other hand, the addition of NBU<sup>n</sup><sub>4</sub>OH to a CH<sub>3</sub>CN

Table 4-I. The equilibrium constants ( $\text{mol}^{-1} \text{ dm}^3$ ) between  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$  and  $[\text{RuL}_1\text{L}_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$  ( $K_1$ ), and between the latter and  $[\text{RuL}_1\text{L}_2(\text{CO})(\text{COO}^-)]^+$  ( $K_2$ )

$L_1$	$L_2$	$K_1$	$K_2$
bpy	bpy	$1.32 \times 10^5$	$2.27 \times 10^4$
bpy	dmbpy	$3.96 \times 10^4$	$9.08 \times 10^3$
dmbpy	dmbpy	$4.41 \times 10^4$	$4.64 \times 10^3$

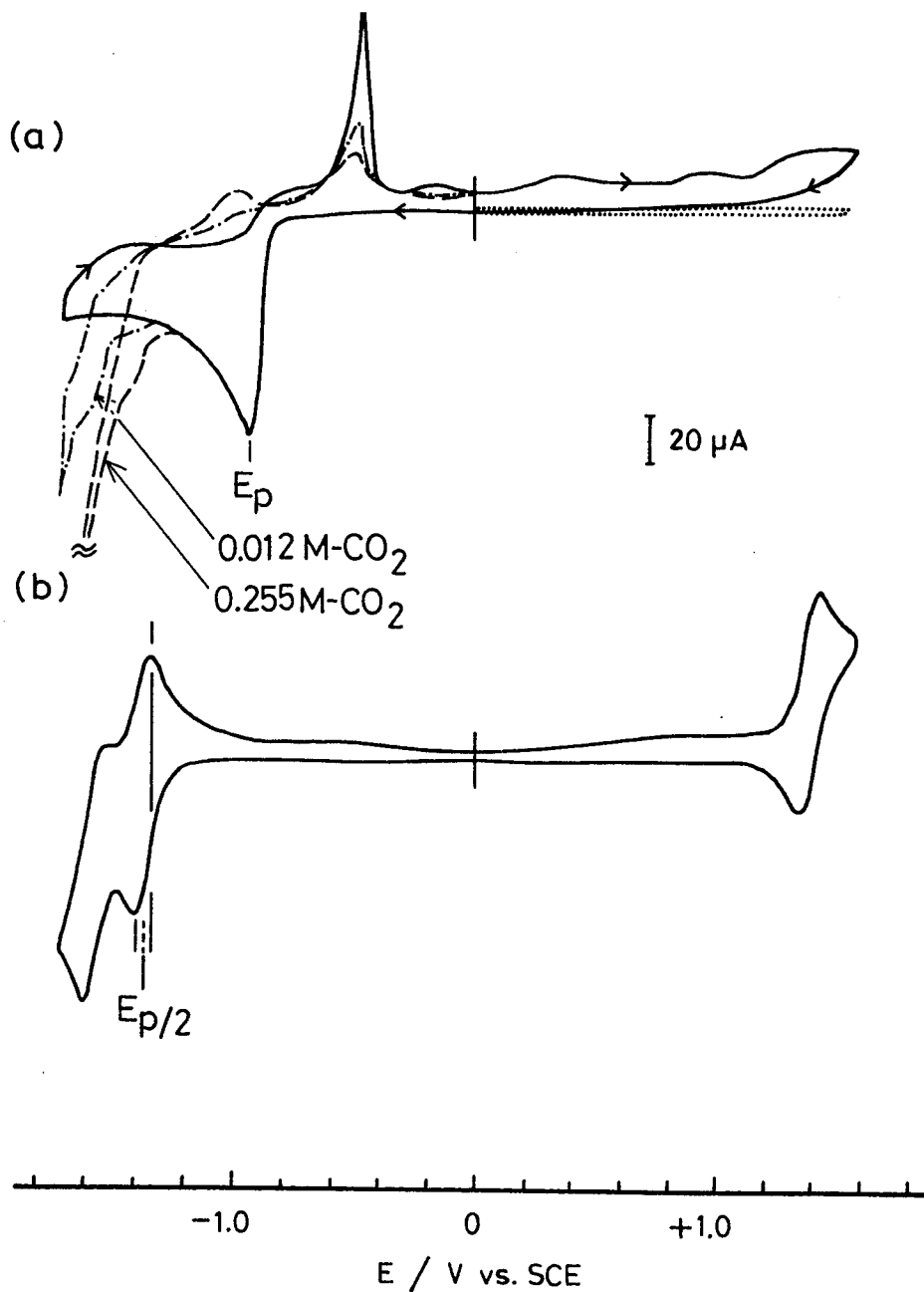


Figure 4-3. Cyclic voltammograms of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  (a) and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  (b) in  $\text{CH}_3\text{CN}$  under  $\text{N}_2$  (— and ..... ) and  $\text{CO}_2$  (— · — and - - -) atmospheres.

Table 4-II. Peak potentials of the irreversible reduction in the cyclic voltammograms of  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$  <sup>a</sup>

L <sub>1</sub>	L <sub>2</sub>	$E_p$ <u>V vs. SCE</u>	Solvent
bpy	bpy	-0.95	DMF
		-1.03	CH <sub>3</sub> CN
bpy	dmbpy	-1.05	DMF
		-1.13	CH <sub>3</sub> CN
dmbpy	dmbpy	-1.05	DMF
		-1.13	CH <sub>3</sub> CN
phen	phen	-1.07	CH <sub>3</sub> CN

<sup>a</sup>  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$   $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>; NBu<sub>4</sub><sup>n</sup>ClO<sub>4</sub> 0.10 mol dm<sup>-3</sup>; sweep rate 0.10 V s<sup>-1</sup>.

solution of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  under  $\text{N}_2$  atmospheres results in disappearance of the cathode peak at  $-1.0 \text{ V vs. SCE}$ , instead there occurs new peaks at ca.  $-1.4$  and  $-1.6 \text{ V vs. SCE}$ . The equimolar and twice molar addition of  $\text{NBu}^n_4\text{OH}$  to  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  produces  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$ , respectively, as confirmed from the fact that the former exhibits the same cyclic voltammogram as the latter. However, the further addition of  $\text{NBu}^n_4\text{OH}$  resulted in decomposition of the ruthenium complex; color of the solution turned to green from orange. The cyclic voltammogram of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  which is generated by twice molar addition of  $\text{NBu}^n_4\text{OH}$  to  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  is shown in Figure 4-3b, which reveals three redox couples. Of those two redox couples around  $-1.4 \text{ V}$  and  $+1.4 \text{ V vs. SCE}$  are pseudo-reversible, whereas the remaining couple around  $-1.6 \text{ V vs. SCE}$  is irreversible. The reduction potentials around  $-1.4$  and  $-1.6 \text{ V vs. SCE}$  agree closely with those in the cyclic voltammograms of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  under a low concentration of  $\text{CO}_2$ , as shown in Figure 4-3a. This result also supports the formation of  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  as an intermediate of the present  $\text{CO}_2$  fixation. The first one-electron reduction potentials of  $[\text{RuL}_1\text{L}_2(\text{CO})(\text{COO}^-)]^+$  ( $\text{L}_1\text{L}_2 = (\text{bpy})_2, (\text{bpy})(\text{dmbpy}), (\text{dmbpy})_2, (\text{phen})_2$ ) also are shifted to negative values with introducing  $\text{dmbpy}$  ligands, as listed in Table 4-III.

**Cyclic Voltammograms of  $\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2$ .**

**Mono-bipyridine**



Table 4-III. Reduction potentials  
of  $[\text{RuL}_1\text{L}_2(\text{CO})(\text{COO}^-)]^+$  <sup>a</sup>

L <sub>1</sub>	L <sub>2</sub>	E <sub>p</sub> /2		Solvent
		V vs. SCE		
bpy	bpy	-1.26	DMF	
		-1.37	CH <sub>3</sub> CN	
bpy	dmbpy	-1.38	DMF	
		-1.45	CH <sub>3</sub> CN	
dmbpy	dmbpy	-1.40	DMF	
		-1.48	CH <sub>3</sub> CN	
phen	phen	-1.38	CH <sub>3</sub> CN	

<sup>a</sup>  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$   $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>;  
 $\text{NBu}_4^{\text{n}}\text{OH}$   $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>;  $\text{NBu}_4^{\text{n}}\text{ClO}_4$   
 $0.10$  mol dm<sup>-3</sup>; sweep rate  $0.10$  V s<sup>-1</sup>.

complexes of rhenium,  $\text{Re}(\text{bpy})(\text{CO})_3\text{X}$  ( $\text{X} = \text{Br}, \text{Cl}$ ), are known to catalyze electrochemical  $\text{CO}_2$  reduction,<sup>3</sup> while no catalytic activity has been reported for the corresponding ruthenium complexes. The cyclic voltammogram of  $\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2$  in  $\text{CH}_3\text{CN}$  exhibits an irreversible cathode peak at  $-1.2 \text{ V vs. SCE}$  and an anode peak weaker than the cathode one at  $-0.4 \text{ V vs. SCE}$  under  $\text{N}_2$  atmospheres, as shown in Figure 4-4. On the other hand, the same complex in  $\text{CH}_3\text{CN}$  under  $\text{CO}_2$  atmospheres displays a strong cathode peak around  $-1.85 \text{ V vs. SCE}$ , which is more negative potential than that of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ , and rather close to the reduction potential ( $-2.0 \text{ V vs. SCE}$ ) of  $\text{CO}_2$  without any catalysts. In view of this result, the  $\text{CO}_2$  activation by  $\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2$  may be effective less than that by  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ . The cyclic voltammogram in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (9:1 v/v) under  $\text{CO}_2$  atmospheres, however, shows a large cathodic current around  $-1.2 \text{ V vs. SCE}$ , which may correspond to  $\text{CO}_2$  reduction. Thus,  $\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2$  may function as a catalyst for the electrochemical  $\text{CO}_2$  reduction, in particular being efficient in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (9:1 v/v).

#### **Electrochemical $\text{CO}_2$ Reductions Catalyzed by Several**

**Ruthenium Complexes.** The  $\text{CO}_2$  reductions were performed in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (4:1 v/v) solutions containing several ruthenium complexes shown in Table 4-IV by the controlled potential electrolysis at  $-1.30 \text{ V vs. SCE}$ . The current densities in the electrolysis are almost the same ( $2 - 3 \text{ mA cm}^{-2}$ ) between the ruthenium complexes with 2,2'-bipyridine and 4,4'-dimethyl-2,2'-

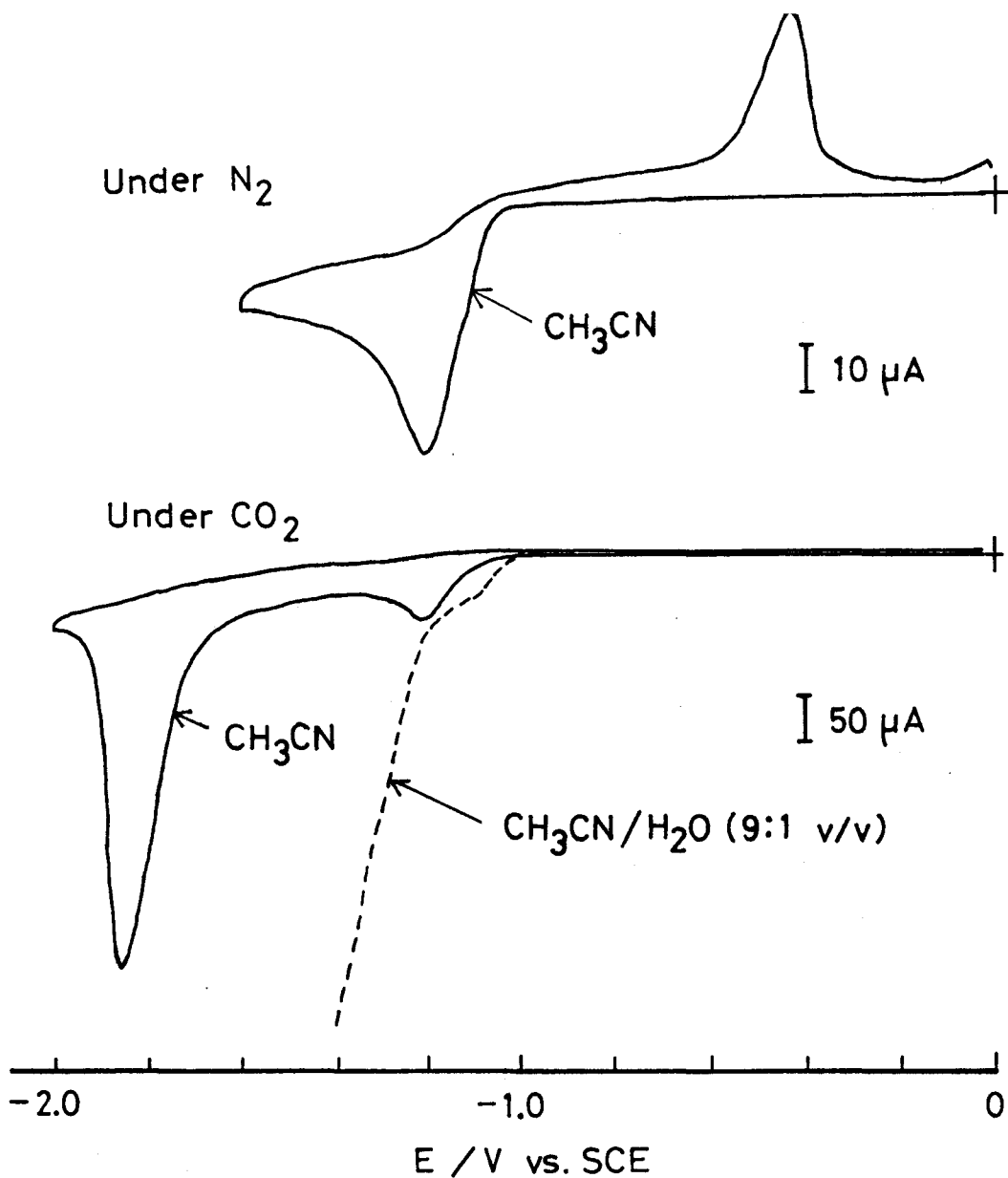


Figure 4-4. Cyclic Voltammograms of  $\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2$  in  $\text{CH}_3\text{CN}$  (—) and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (9:1 v/v) (---) under  $\text{N}_2$  and  $\text{CO}_2$  atmospheres.

Table 4-IV. The electrochemical CO<sub>2</sub> reductions catalyzed by several ruthenium complexes in MeCN/H<sub>2</sub>O (4:1 v/v)<sup>a</sup>

Catalyst	Product <sup>b</sup> / μmol
	CO
[Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	209 (67.2%)
[Ru(bpy)(dmbpy)(CO) <sub>2</sub> ] <sup>2+</sup>	223 (71.8%)
[Ru(dmbpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	203 (65.3%)
[Ru(phen) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	191 (61.5%)
[Ru(phen) <sub>2</sub> (CO)Cl] <sup>+</sup>	207 (66.6%)
Ru(bpy)(CO) <sub>2</sub> Cl <sub>2</sub>	273 (87.8%)
Ru(dmbpy)(CO) <sub>2</sub> Cl <sub>2</sub>	205 (66.0%)

<sup>a</sup> -1.30 V vs. SCE; an Hg electrode (3.3 cm<sup>2</sup>); 60 coulombs consumed. <sup>b</sup> The current efficiency (%) in parentheses.

bipyridine as catalysts, while they are influenced by stirring speed. The electrochemical CO<sub>2</sub> reduction proceeds catalytically in the presence of either ruthenium complex, while the rate of reductions is somewhat slow when the ruthenium complexes with 1,10-phenanthroline are used as catalysts. The reduction product is only carbon monoxide even in either case, and the amount is independent of the catalyst (Table 4-IV).

The electrochemical CO<sub>2</sub> reduction also proceeds in CH<sub>3</sub>OH, while the current densities are relatively low (ca. 0.5 - 1.0 mA cm<sup>-2</sup>). In the reduction upon using [Ru(phen)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> or [Ru(phen)(CO)Cl]<sup>+</sup>, CH<sub>3</sub>CN/CH<sub>3</sub>OH (4:1 v/v) is used as a solvent due to poor solubility of these ruthenium complexes to CH<sub>3</sub>OH. The reduction products in CH<sub>3</sub>OH, however, are not only carbon monoxide but also formic acid, as shown in Table 4-V. The amounts of these products are dependent on the catalyst; carbon monoxide increases and formic acid decreases in the amount with increasing the donor property of the ligand. For instance, the amount of carbon monoxide generated increases in the order [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> < [Ru(bpy)(dmbpy)(CO)<sub>2</sub>]<sup>2+</sup> < [Ru(dmbpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>, whereas the amount of formic acid produced is opposite. Similar increasing amount of carbon monoxide was observed as follows; Ru(bpy)(CO)<sub>2</sub>Cl<sub>2</sub> < Ru(dmbpy)(CO)<sub>2</sub>Cl<sub>2</sub> .

**Mechanisms of CO<sub>2</sub> Reduction.** The mechanisms for the electrochemical CO<sub>2</sub> reductions using [Ru(bpy)(dmbpy)(CO)<sub>2</sub>]<sup>2+</sup> and [Ru(dmbpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> as catalysts may be the same as that by using

Table 4-V. The electrochemical CO<sub>2</sub> reductions catalyzed by the ruthenium complexes in MeOH<sup>a</sup>

Catalyst	Products <sup>b</sup> / μmol	
	CO	HCOO <sup>-</sup>
[Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	81 (26.1%)	154 (49.5%)
[Ru(bpy)(dmbpy)(CO) <sub>2</sub> ] <sup>2+</sup>	106 (34.2%)	123 (39.8%)
[Ru(dmbpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	139 (44.7%)	101 (32.5%)
[Ru(phen) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup> <sup>c</sup>	108 (34.7%)	76 (24.5%)
[Ru(phen) <sub>2</sub> (CO)Cl] <sup>+</sup> <sup>c</sup>	123 (39.6%)	40 (12.9%)
Ru(bpy)(CO) <sub>2</sub> Cl <sub>2</sub>	85 (27.3%)	117 (37.7%)
Ru(dmbpy)(CO) <sub>2</sub> Cl <sub>2</sub>	122 (39.2%)	83 (26.8%)

<sup>a</sup> -1.30 V vs. SCE; an Hg electrode (3.3 cm<sup>2</sup>); 60 coulombs consumed. <sup>b</sup> The current efficiency (%) in parentheses.

<sup>c</sup> In MeCN/MeOH (4:1 v/v).

$[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  as a catalyst, as described in chapter 2. The change of products distribution may be associated with the equilibrium reactions among  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$ ,  $[\text{RuL}_1\text{L}_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ , and  $[\text{RuL}_1\text{L}_2(\text{CO})(\text{COO}^-)]^+$  ( $\text{L}_1, \text{L}_2 = \text{bpy}, \text{dmbpy}, \text{phen}$ ); the equilibrium concentration of  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$  becomes small with replacing the dmbpy ligand for  $\text{L}_1$  and  $\text{L}_2$  as bpy, because of the donor property of the  $\text{CH}_3$  group. Thus, the amount of carbon monoxide generated becomes large with introducing the dmbpy ligand when the electrochemical reduction of  $\text{CO}_2$  was conducted in  $\text{CH}_3\text{OH}$ .

The electrochemical  $\text{CO}_2$  reduction catalyzed by  $\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2$  or  $\text{Ru}(\text{dmbpy})(\text{CO})_2\text{Cl}_2$  gives a result similar to that catalyzed by the ruthenium bis(bipyridine) complexes. In order to obtain the information on active species in the catalytic system, electrochemical spectra of  $\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2$  and  $\text{Ru}(\text{dmbpy})(\text{CO})_2\text{Cl}_2$  were measured in  $\text{CH}_3\text{CN}$  to result in the decomposition of the ruthenium complexes. On the other hand, the measurement of electronic absorption spectra of  $\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2$  and  $\text{Ru}(\text{dmbpy})(\text{CO})_2\text{Cl}_2$  in  $\text{H}_2\text{O}$  has indicated that these complexes irreversibly react with  $\text{OH}^-$  to lead the dissociation of the chloride or CO ligand. Thus, further study may required for elucidating active species in the present  $\text{CO}_2$  reduction by monobipyridine catalysts.

In conclusion, the amounts of carbon monoxide become large with introducing the dmbpy ligand in the electrochemical  $\text{CO}_2$  reductions catalytically by  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$  ( $\text{L}_1\text{L}_2 = (\text{bpy})_2, (\text{bpy})(\text{dmbpy}), (\text{dmbpy})_2$ ) in  $\text{CH}_3\text{OH}$ . It is attributed to that the equilibrium constants among  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$ ,  $[\text{RuL}_1\text{L}_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ ,

and  $[\text{RuL}_1\text{L}_2(\text{CO})(\text{COO}^-)]^+$  become small with replacing the dmbpy ligand for  $\text{L}_1$  and  $\text{L}_2$  as bpy, because of the donor property of the  $\text{CH}_3$  group. This finding is first example which observes the ligand effects toward the products selectivity for electrochemical  $\text{CO}_2$  reductions catalyzed by transition metal complexes.

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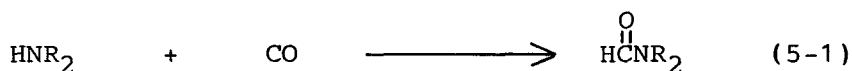
## Chapter 5

### Generation of N,N-Dimethylformamide by the Electrochemical CO<sub>2</sub> Reduction with (CH<sub>3</sub>)<sub>2</sub>NH, Catalyzed by a Ruthenium Complex

#### 5-1 Introduction

Although electrochemical CO<sub>2</sub> reductions catalyzed by transition metal complexes have extensively been studied in recent years, the reduction products in most cases are limited to CO and/or HCOO<sup>-</sup>. The conversion of CO<sub>2</sub> to organic molecules other than HCOO<sup>-</sup>, therefore, is highly desired in the viewpoint of utilization of CO<sub>2</sub>.<sup>1</sup>

Transition metal complexes are known to catalyze the thermal reaction of carbon monoxide with dialkyl amine to give formamide (eq. 5-1).<sup>2</sup> As described in previous chapters, some ruther-



nium(II) complexes have successfully used as catalysts in the electrochemical conversion of CO<sub>2</sub> to CO and/or HCOO<sup>-</sup>. This chapter described the generation of N,N-dimethylformamide by the electrochemical CO<sub>2</sub> reduction with (CH<sub>3</sub>)<sub>2</sub>NH, catalyzed by [Ru-(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>, including the identification of reaction interme-

diates.

## 5-2 Experimental Sections

**Materials.** An anhydrous  $\text{CH}_3\text{CN}$  solution of dimethylamine was prepared as follow; commercially available dimethylamine was heated in the presence of  $\text{NaOH}$  under  $\text{N}_2$  atmospheres to give dry dimethylamine vapor, which was bubbled into anhydrous  $\text{CH}_3\text{CN}$  through  $\text{CaCl}_2$  tube. The concentration of dimethylamine in  $\text{CH}_3\text{CN}$  was determined by titration.  $\text{Na}_2\text{SO}_4$  was heated at  $150^\circ\text{C}$  for one day before use.

**Electrochemical  $\text{CO}_2$  Reductions in the Presence of Dimethylamine.** The electrochemical reduction was performed with the same electrolysis cell as that described in Chapter 3. An  $\text{CH}_3\text{CN}$  solution containing ruthenium complexes,  $(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$ , and  $\text{Na}_2\text{SO}_4$  was bubbled with  $\text{CO}_2$  for 30 min, followed by the addition of an  $\text{CH}_3\text{CN}$  solution of dimethylamine. The resulting solution was further bubbled with  $\text{CO}_2$  for ca. 5 min. The diterminations of  $\text{CO}$ ,  $\text{H}_2$  and  $\text{HCOO}^-$  produced in the electrochemical reaction were performed by the methods described in Chapter 3. DMF was analyzed with a Shimadzu GC-7A gaschromatograph equipped with FID using a 2 m column filled with Chromosorb 103 under  $\text{N}_2$  carrier gas.

### 5-3 Results and discussion

**Formation of the carbamoyl complex,  $[\text{Ru}(\text{bpy})_2(\text{CO})-\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$ , as a Reaction Intermediate.** In the amide synthesis by the reaction of amine with carbon monoxide, catalyzed by transition metal complexes under high pressures and temperatures, carbamoyl metal complexes have been considered as important precursors.<sup>3</sup> Thus, the reaction of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  with  $(\text{CH}_3)_2\text{NH}$  was monitored by IR spectra of the acetonitrile solutions to examine the possibility of the formation of such complexes. The IR spectrum of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  (13.0 mmol dm<sup>-3</sup>) exhibits two  $\nu(\text{C}\equiv\text{O})$  bands at 2050 and 2101 cm<sup>-1</sup> (a broken line in Figure 5-1), both of which completely disappear upon the addition of  $(\text{CH}_3)_2\text{NH}$  (26.0 mmol dm<sup>-3</sup>), instead two new bands appear at 1947 and 1624 cm<sup>-1</sup> (a solid line in Figure 5-1). The removal of  $(\text{CH}_3)_2\text{NH}$  from the solution by bubbling N<sub>2</sub> or by evaporation under reduced pressures followed by dissolution in acetonitrile resulted in regeneration of the IR spectrum of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ , suggesting that  $(\text{CH}_3)_2\text{NH}$  reversibly reacts with  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ . The 1947 and 1624 cm<sup>-1</sup> bands appeared in the presence of  $(\text{CH}_3)_2\text{NH}$  may be assigned to the  $\nu(\text{C}\equiv\text{O})$  and  $\nu(\text{C}=\text{O})$ , respectively, of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$ , since carbamoyl metal complexes was reported to exhibit the  $\nu(\text{C}=\text{O})$  bands in the 1500 - 1700 cm<sup>-1</sup> range.<sup>4</sup>

The electronic spectra of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  are drastically changed by the addition of  $(\text{CH}_3)_2\text{NH}$  as shown in Figure 5-2; two

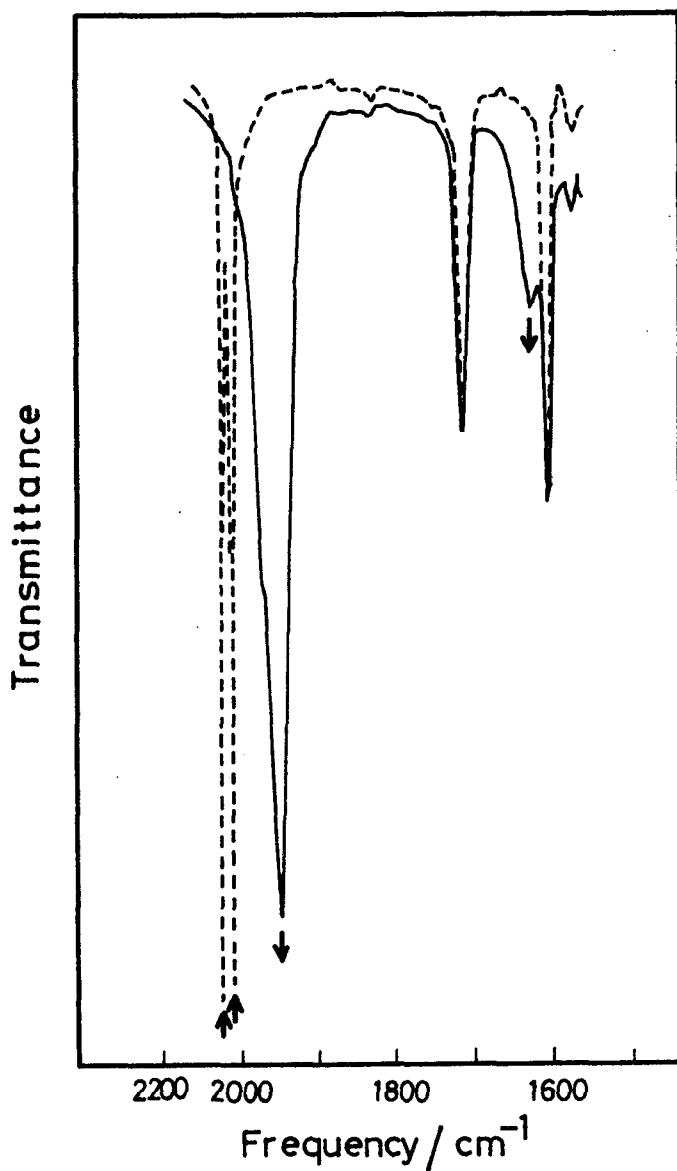


Figure 5-1. FT-IR spectra of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in acetonitrile in the presence (—) and absence (----) of  $(\text{CH}_3)_2\text{NH}$ .

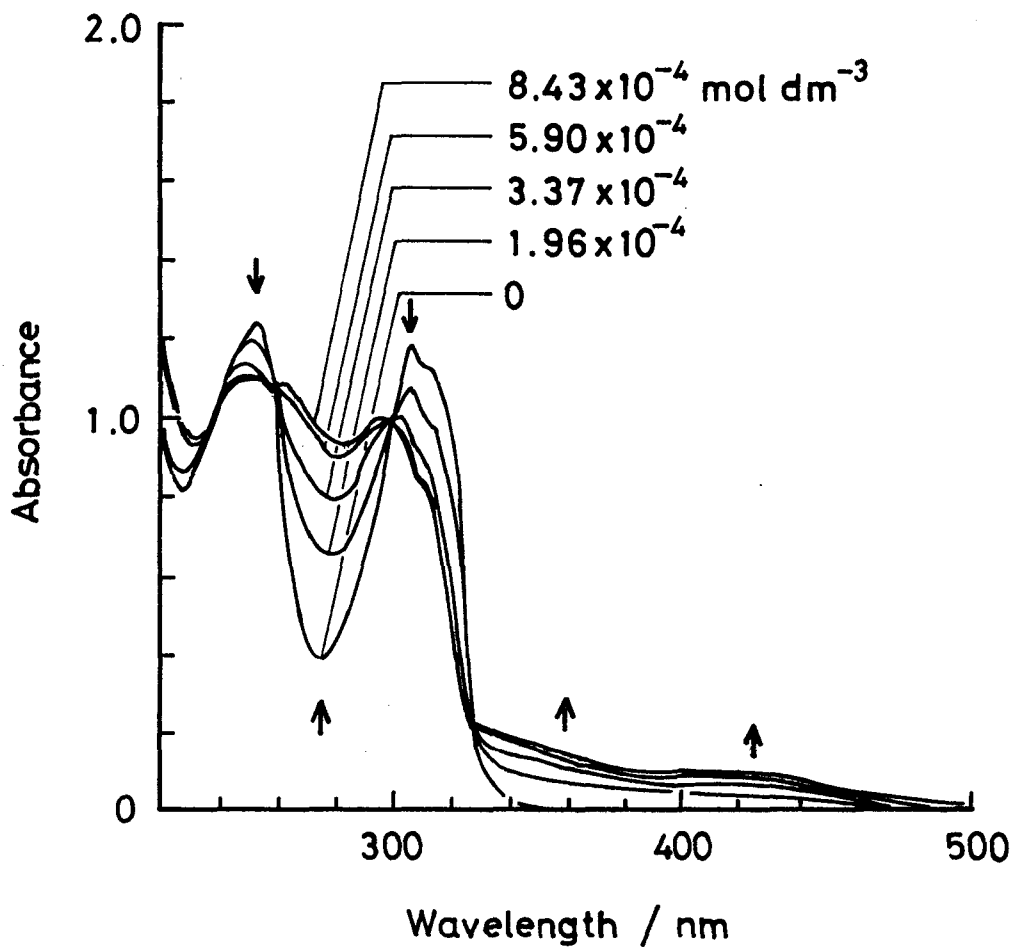


Figure 5-2. Electronic absorption spectra of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $4.32 \times 10^{-5} \text{ mol dm}^{-3}$ ) in  $\text{CH}_3\text{CN}$  in the presence of  $(\text{CH}_3)_2\text{NH}$  (0,  $1.96 \times 10^{-4}$ ,  $3.37 \times 10^{-4}$ ,  $5.90 \times 10^{-4}$ ,  $8.43 \times 10^{-4} \text{ mol dm}^{-3}$ ) at  $25^\circ\text{C}$ .

absorption bands of the dicarbonyl complex at 253 and 307 nm disappear, and four bands newly appear at 263, 295, 357 and 425 nm. The changes in the electronic spectra and the IR spectra are essentially the same as the spectral changes of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  under alkaline conditions, where the carbonyl group of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  undergoes nucleophilic attack with  $\text{OH}^-$  to afford a hydroxy carbonyl complex  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ . Therefore,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$  may be formed by nucleophilic attack of  $(\text{CH}_3)_2\text{NH}$  to a carbonyl group of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ .

The formation of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$  is supported also from the  $^1\text{H}$  NMR spectrum of a mixture of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $66 \text{ mmol dm}^{-3}$ ) with  $(\text{CH}_3)_2\text{NH}$  ( $132 \text{ mmol dm}^{-3}$ ) in acetonitrile- $\text{d}_3$ , which shows a singlet signal at  $\delta$  2.85 (Figure 5-3) as well as the methyl proton signals of  $(\text{CH}_3)_2\text{NH}_2^+$  ( $\delta$  3.80) and  $(\text{CH}_3)_2\text{NH}$  ( $\delta$  2.43) at room temperature. The  $\delta$  2.85 signal may be assigned to the N- $\text{CH}_3$  proton of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$ , since it becomes broaden with lowering the temperature and splits into two signals with the same intensity below  $-30^\circ\text{C}$  (Figure 5-3) owing to the restriction of free rotation around the N-C bond. Several attempts to isolate  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$  have been unsuccessful to recover the starting complex  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$ . This may be due to the fact that  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$  exists as an equilibrium mixture with  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in acetonitrile in the presence of  $(\text{CH}_3)_2\text{NH}$ , as expressed by eq. 5-2. The equilibrium constant for eq. 5-2 was

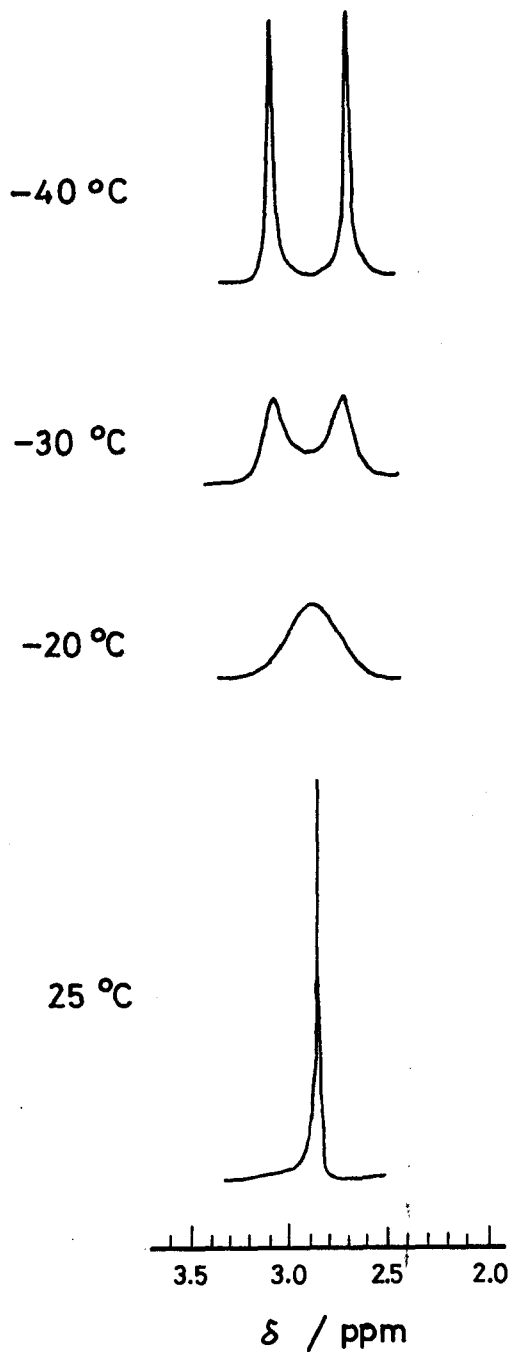
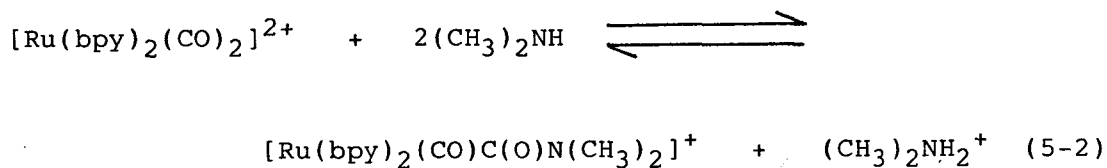


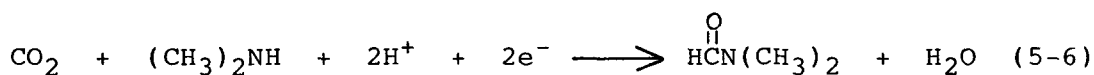
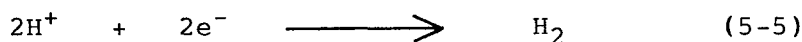
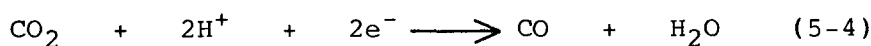
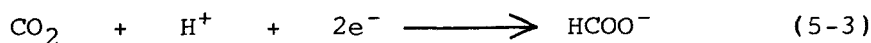
Figure 5-3. Temperature dependence of the methyl proton signals of  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$  in  $\text{CD}_3\text{CN}$ .





determined as  $1.67 \times 10^7 \text{ mol}^{-2} \text{ dm}^6$  at  $25^\circ\text{C}$  from the change of electronic absorption spectra of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in the presence of various amounts of  $(\text{CH}_3)_2\text{NH}$  in acetonitrile.

**Generation of DMF and mechanisms of the electrochemical  $\text{CO}_2$  Reduction.** The controlled potential electrolysis was performed on an Hg working electrode at  $-1.30 \text{ V vs. SCE}$  for a  $\text{CO}_2$ -saturated acetonitrile solution containing  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ,  $\text{Bu}^n_4\text{NClO}_4$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$  and  $\text{Na}_2\text{SO}_4$  as a catalyst, an electrolyte, a substrate, a proton source, and dehydration chemicals, respectively. As the result, two-electron reductions of  $\text{CO}_2$  take place to produce not only  $\text{HCOO}^-$ ,  $\text{CO}$ , and  $\text{H}_2$  but also DMF (eqs. 5-3 - 5-6). The amounts of these products increase



linearly with increasing the electricity consumed in the reduction, and the turnover number for the formation of DMF is more than 10 (based on the amount of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ) at the consumption of 75 coulombs, as depicted in Figure 5-4. The current efficiency for the formation of  $\text{HCOO}^-$ ,  $\text{CO}$ ,  $\text{H}_2$ , and DMF were 75.7, 1.0, 0.7, and 21.4%, respectively, suggesting that any reactions other than eqs. 5-3 - 5-6 hardly take place. In the absence of  $\text{Na}_2\text{SO}_4$ , the current efficiency for the formation of DMF gradually decreased with the progress of the reduction, since the adduct formation between  $(\text{CH}_3)_2\text{NH}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  may strongly be hindered by  $\text{H}_2\text{O}$  formed in the reaction of eqs. 5-4 and 5-6.

Scheme 5-I shows a possible catalytic cycle for the present reaction. As described in the previous chapters,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  undergoes a simultaneous two electron reduction to give  $[\text{Ru}(\text{bpy})_2(\text{CO})]^0$  with liberating a single CO molecule in the absence of  $(\text{CH}_3)_2\text{NH}$ . The penta-coordinated Ru(0) complex thus formed reacts with  $\text{CO}_2$  to yield  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$ , which exists as an equilibrium mixture with  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ; the amount of each species depends on the proton concentration in the reaction mixture, and the latter two are reduced with two electrons to produce  $\text{HCOO}^-$  and  $\text{CO}$ , respectively. The acidity of  $(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$  used as a proton source in the present study is so low that the conversion from  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$  to  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  hardly occurs. Thus, the formation of  $\text{HCOO}^-$  may be predominant. In the presence

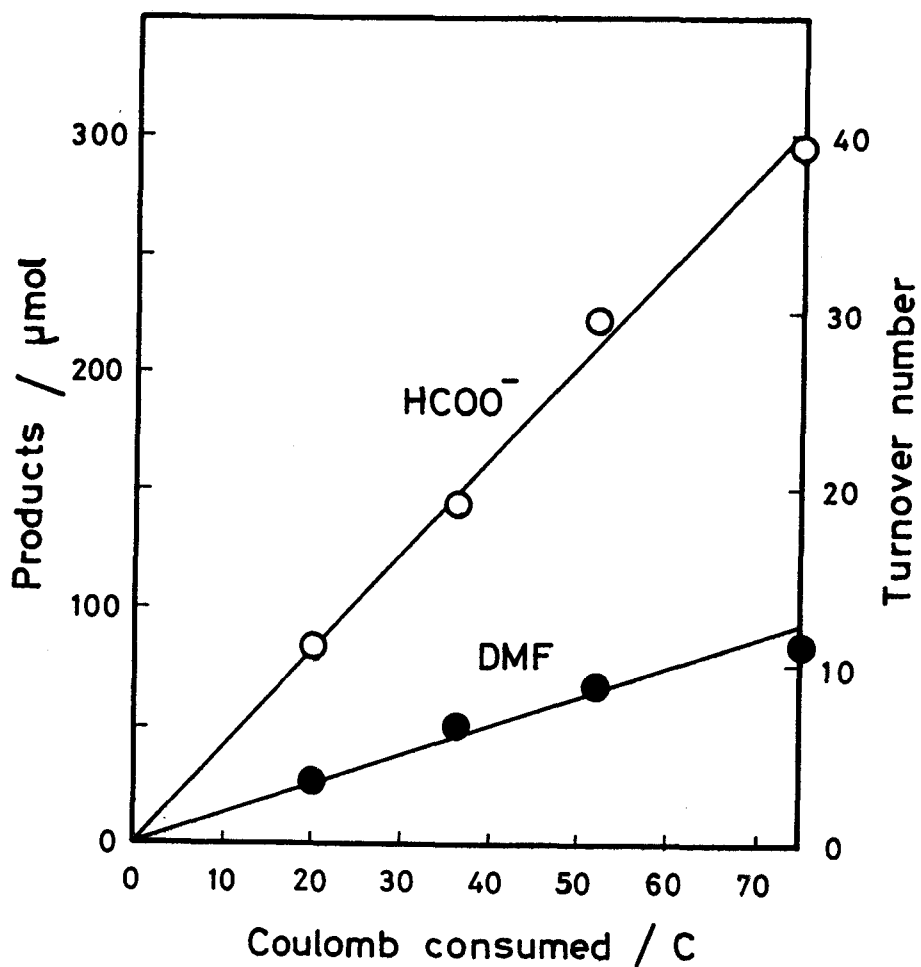
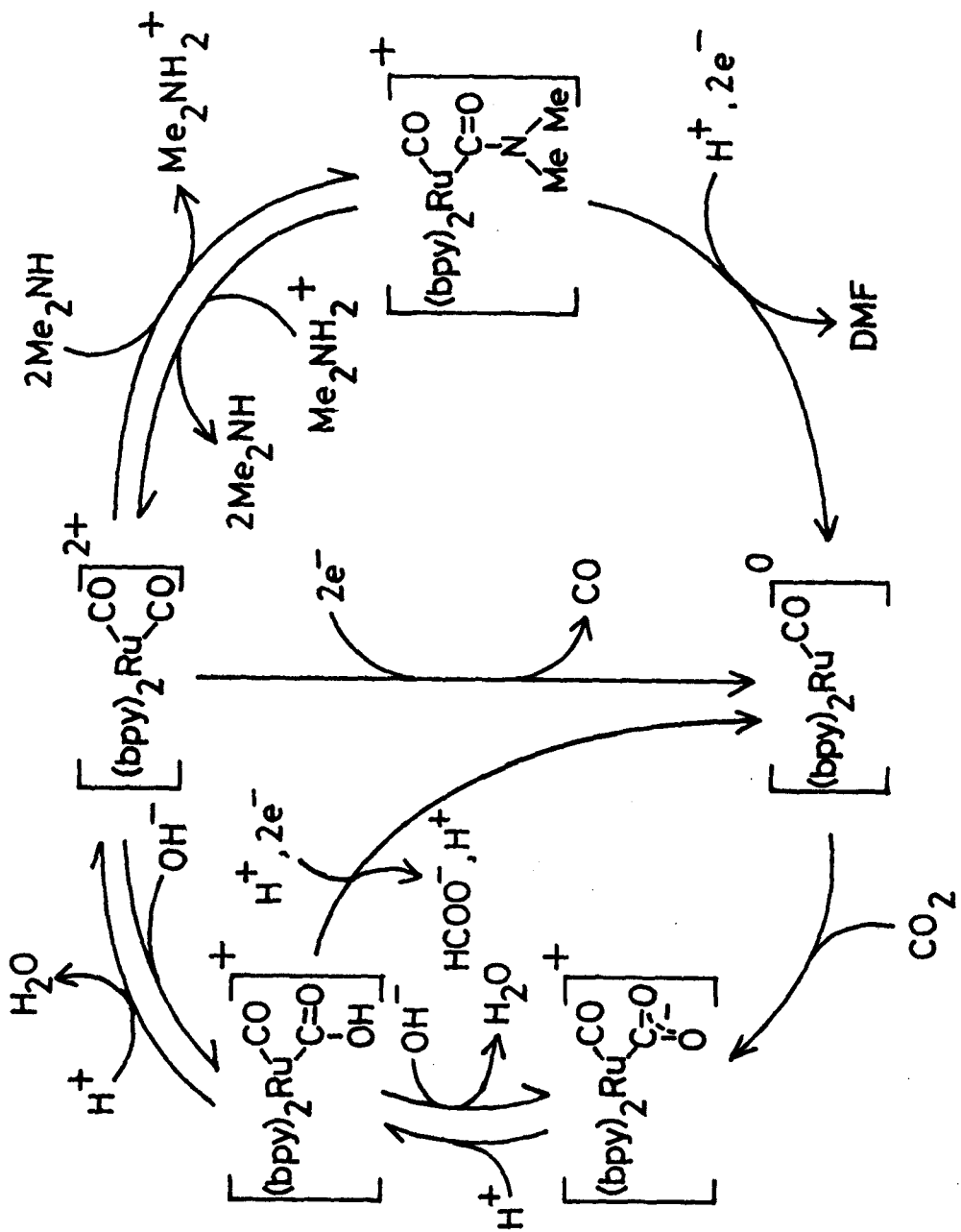


Figure 5-4. Amounts of the products in the electrolysis (-1.30 V vs. SCE) of a CO<sub>2</sub>-saturated acetonitrile solution containing [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, NBu<sup>n</sup><sub>4</sub>ClO<sub>4</sub>, (CH<sub>3</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>2</sub>NH·HCl and Na<sub>2</sub>SO<sub>4</sub> at 30°C.

Scheme 5-I



of  $(\text{CH}_3)_2\text{NH}$ ,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  may effectively react with the amine to produce  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$ , which undergoes two-electron reduction to afford DMF with regenerating the penta-coordinated Ru(0) species  $[\text{Ru}(\text{bpy})_2(\text{CO})]_0$ . Possibility of the DMF formation in the thermal reaction between  $\text{HCOO}^-$  (or CO) and  $(\text{CH}_3)_2\text{NH}$  may be excluded by the fact that no DMF has been formed in the reaction of  $(\text{CH}_3)_2\text{NH}$  with either  $\text{HCOOH}$  or CO in the presence of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  at  $30^\circ\text{C}$ .

#### 5-4 References

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## Chapter 6

### Photochemical and Catalytic Reduction of CO<sub>2</sub> in the [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> / [Ru(bpy)<sub>3</sub>]<sup>2+</sup> / Triethanolamine / N,N-Dimethylformamide System

#### 6-1 Introduction

Photochemical CO<sub>2</sub> fixation is especially of interest in connection with biological photosynthetic systems,<sup>1</sup> and is desired also in terms of construction of economically efficient and clean systems such as utilization of solar energy.<sup>2-13</sup> The photochemical CO<sub>2</sub> reductions reported so far are almost carried out in the system composed of photosensitizer/catalyst/electron donor, where [Ru(bpy)<sub>3</sub>]<sup>2+</sup> is widely used as a photosensitizer.<sup>2-7</sup>

There have been three conflicting reports in those systems containing [Ru(bpy)<sub>3</sub>]<sup>2+</sup>; (i) the irradiation of light ( $\lambda > 320$  nm) to a CO<sub>2</sub>-saturated TEOA/DMF solution containing [Ru(bpy)<sub>3</sub>]<sup>2+</sup> ( $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>) and MV<sup>2+</sup> has been reported to produce HCOO<sup>-</sup>.<sup>2</sup> (ii) HCOO<sup>-</sup> has, however, been suggested to come from the decomposition of TEOA based on <sup>13</sup>C nmr investigations.<sup>14</sup> On the other hand, (iii) Lehn *et al.* has demonstrated the selective formation of H<sup>13</sup>COO<sup>-</sup> in similar photochemical ( $\lambda > 400$  nm) <sup>13</sup>CO<sub>2</sub> reductions using a very high concentration of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> ( $1.1 \times 10^{-2}$  mol dm<sup>-3</sup>) in TEOA/DMF even in the absence of MV<sup>2+</sup>.<sup>3</sup> Such a

conflict may be solved by consideration that the actual catalyst in the CO<sub>2</sub> reduction may be neither [Ru(bpy)<sub>3</sub>]<sup>2+</sup> nor MV<sup>2+</sup> but a ruthenium bis(bipyridine) complex resulting from dissociation of a bpy ligand of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>. However, the photochemical CO<sub>2</sub> reductions catalyzed by ruthenium bis(bipyridine) complexes have never been investigated.

This chapter describes the details of the photochemical CO<sub>2</sub> reduction catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in the presence of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as a photosensitizer and TEOA as an electron donor.

## 6-2 Experimental Section

**Material.** [Ru(phen)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> was prepared according to the literature.<sup>15</sup> The preparation of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O, and Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O were described in the previous chapters. N,N-dimethylformamide (DMF) was purified by azeotropic distillation with benzene, followed by distillation under reduced pressures, and stored under an N<sub>2</sub> atmosphere. Triethanolamine (TEOA), d<sup>7</sup>-DMF, and Na<sub>2</sub><sup>13</sup>CO<sub>3</sub> were purchased from Wako Pure Chemicals and used without further purification. Potassium ferrioxalate<sup>16</sup> used as an actinometer was purified by recrystallization from hot water.

**Photochemical CO<sub>2</sub> Reduction.** A TEOA/DMF (1:4 v/v; 5 cm<sup>3</sup>) mixture containing fixed amounts of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O and [Ru-



$(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  was bubbled with  $\text{CO}_2$  through a septum cap attached to the top of a pyrex tube ( $32 \text{ cm}^3$ ) with teflon tube for 30 min. The photochemical reduction of  $\text{CO}_2$  thus saturated in the solution was initiated by irradiating light with a 300 W Hg lamp through a cut-off chemical filter (1 cm) prepared  $0.50 \text{ mol dm}^{-3}$  of  $\text{CuSO}_4$  ( $\lambda > 320 \text{ nm}$ ). After the lapse of a fixed time,  $0.1 \text{ cm}^3$  portions of gas and the solution were sampled from the gaseous and liquid phases, respectively, in the flask through the septum cap with syringe techniques. Quantitative analysis of the gas was performed on a Shimazu gas chromatograph GC-3BT with a 2 m column filled with Molecular Sieve 13X at 343 K using He ( $40 \text{ cm}^3 \text{ min}^{-1}$ ) as a carrier gas.  $\text{HCOO}^-$  formed in the solution was determined with a Shimazu Isotachophoretic Analyzer IP-2A using a mixture of  $\beta$ -alanine ( $0.02 \text{ mol dm}^{-3}$ ) and HCl ( $0.01 \text{ mol dm}^{-3}$ ) in an aqueous Triton X-100 (0.2 vol%) solution, and caproic acid ( $0.01 \text{ mol dm}^{-3}$ ) in  $\text{H}_2\text{O}$  as leading and terminal electrolytes, respectively.

$^{13}\text{C}$  nmr experiments were performed in a  $^7\text{d}$ -DMF/DMF/TEOA (5:3:2 v/v,  $1.0 \text{ cm}^3$ ) solution containing an equal amount ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$  in an nmr tube (i.d. = 1.0 cm). The tube was thoroughly flushed with He with teflon tube to remove air, and then  $^{13}\text{CO}_2$  prepared by addition of  $\text{H}_2\text{SO}_4$  (0.10 N) to an aqueous solution of 99%  $\text{Na}_2^{13}\text{CO}_3$  (1.0 g) was bubbled into the solution through a glass tube packed with  $\text{CaCl}_2$ . After photoirradiation for 20 h, the  $^{13}\text{C}$  nmr spectra of the solution were measured at 15.3 MHz using the pulse fourier

technique with a JEOL EX-60 spectrometer against TMS as the internal standard.

**Quantum Yield Determination.** Quantum yields of the photochemical CO<sub>2</sub> reduction were determined in a square quartz cuvette (1.0 cm). After CO<sub>2</sub> was bubbled into the quartz cuvette containing the test solution (2.0 cm<sup>3</sup>) with Teflon tube for 30 min, the solution was photoirradiated with a 300 W Xenon lamp (Ushio Model U1-501) through a Toshiba glass filter Y-43 transmitting light of  $\lambda > 400$  nm for 5, 10, and 15 min. The rate of the photochemical CO<sub>2</sub> reduction was determined by the analysis of the reduction products in the gaseous (CO) and liquid phases (HCOO<sup>-</sup>). Potassium ferrioxalate was used as a standard actinometer for the quantum yield determinations on the photochemical CO<sub>2</sub> reductions. Calculations of the quantum yield were performed according to the literature.<sup>17</sup>

### 6-3 Results and Discussion

Photochemical CO<sub>2</sub> reduction catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in the presence of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in TEOA/DMF. An irradiation of light ( $\lambda > 400$  nm) to a CO<sub>2</sub>-saturated TEOA/DMF (1:4 v/v) solution containing [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (1.1 x 10<sup>-2</sup> mol dm<sup>-3</sup>) has produced 997  $\mu$ mol of HCOO<sup>-</sup> for 20 h, while the photochemical CO<sub>2</sub> reduction using a low concentration of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (5.0 x 10<sup>-4</sup> mol dm<sup>-3</sup>)

afforded only 7  $\mu\text{mol}$  of  $\text{HCOO}^-$  in the same solvent (entry 1 in Table 6-I). The addition of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  to the low concentration solution of  $[\text{Ru}(\text{bpy})_3]^{2+}$  brings about a drastic change of the formation of  $\text{HCOO}^-$ ; the amount of  $\text{HCOO}^-$  increases with increasing the concentration of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  (entry 2 - 6 in Table 6-I), and attains the maximum value 394  $\mu\text{mol}$  when the concentration of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  is the same as that of  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) (entry 5 in Table 6-I). A further increase of the  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  concentration in the solution, however, results in a gradual decrease of the amount of  $\text{HCOO}^-$  (entry 7 and 8 in Table 6-I). In addition, no photochemical  $\text{CO}_2$  reduction with  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  takes place in the absence of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (entry 9 in Table 6-I). These results reveal that both  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  are essential components to proceed an effective photochemical  $\text{CO}_2$  reduction. Similar photochemical  $\text{CO}_2$  reductions take place also in a TEOA/ $\text{CH}_3\text{CN}$  (1:4 v/v) solution, though the amount of  $\text{HCOO}^-$  formed is low compared with that in TEOA/DMF (entry 10 - 12 in Table 6-I).

The photochemical  $^{13}\text{CO}_2$  reduction was carried out also in a  $^{13}\text{CO}_2$ -saturated  $d^7$ -DMF/DMF/TEOA (5:3:2 v/v) solution containing an equal amount of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ). The  $^{13}\text{C}$  nmr spectrum of the reaction mixture obtained after irradiation of light ( $\lambda > 320 \text{ nm}$ ) for 20 h clearly indicates the formation of  $\text{H}^{13}\text{COO}^-$  ( $\delta 168.1 \text{ ppm}$ ) together with hydroxyacetaldehyde ( $\delta 93.0 \text{ ppm}$ )<sup>3</sup> and diethanolamine<sup>18</sup> as

**Table 6-I.** Photochemical CO<sub>2</sub> reductions in CO<sub>2</sub>-saturated TEOA/DMF (1:4 v/v, 5 cm<sup>3</sup>) containing [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> under irradiation of light (λ > 320 nm)<sup>a</sup> for 20 h

Entry	Concentration / mol dm <sup>-3</sup>		HCOO <sup>-</sup> / μmol
	[Ru(bpy) <sub>3</sub> ] <sup>2+</sup>	[Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	
1	5.0 x 10 <sup>-4</sup>	0	7
2	5.0 x 10 <sup>-4</sup>	1.0 x 10 <sup>-5</sup>	186
3	5.0 x 10 <sup>-4</sup>	5.0 x 10 <sup>-5</sup>	258
4	5.0 x 10 <sup>-4</sup>	1.0 x 10 <sup>-4</sup>	315
5	5.0 x 10 <sup>-4</sup>	5.0 x 10 <sup>-4</sup>	394
6	5.0 x 10 <sup>-4</sup>	1.0 x 10 <sup>-3</sup>	324
7	5.0 x 10 <sup>-4</sup>	1.5 x 10 <sup>-3</sup>	265
8	5.0 x 10 <sup>-4</sup>	2.0 x 10 <sup>-3</sup>	265
9	0	5.0 x 10 <sup>-4</sup>	0
10 <sup>b</sup>	5.0 x 10 <sup>-4</sup>	0	1
11 <sup>b</sup>	5.0 x 10 <sup>-4</sup>	5.0 x 10 <sup>-4</sup>	93
12 <sup>b</sup>	0	5.0 x 10 <sup>-4</sup>	0

<sup>a</sup> 300 W-Hg lamp. <sup>b</sup> In TEOA/CH<sub>3</sub>CN (1:4 v/v).

decomposition products of TEOA, as shown in Figure 6-1. The amount of  $\text{H}^{13}\text{COO}^-$  determined by the signal intensity at  $\delta$  168.1 was consistent with that determined by an isotachophoretic analyzer. Thus, the  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}/\text{TEOA}$  system effectively reduces  $\text{CO}_2$  to produce selectively  $\text{HCOO}^-$  under irradiation of light in DMF. Plots of the amount of  $\text{HCOO}^-$  formed against time under the optimum conditions in the present study (entry 5 in Table 6-I) displays a gradual deviation from a linear relation, as shown in Figure 6-2, which suggests that the system slowly loses the catalytic activity for the photochemical  $\text{CO}_2$  reduction. This is compatible with the formation of a black precipitate during the photochemical  $\text{CO}_2$  reduction. The formation of such a black precipitate was observed also when the photochemical  $\text{CO}_2$  reduction was conducted with the mole ratio of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}$  being larger than 1. Thus, the decrease in the rate of the  $\text{HCOO}^-$  formation with the lapse of time (Figure 6-2) may be caused not only by the gradual decomposition of the catalyst but also by the inner filter effect due to dispersion of the black solid in solutions.

The quantum yield for the photochemical  $\text{CO}_2$  reduction under the concentration of  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) increases with increasing the concentration of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  up to  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ , and reaches to the constant value 14%, as shown in Figure 6-3, which indicates that 10 mole % of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  per  $[\text{Ru}(\text{bpy})_3]^{2+}$  suffices in the amount for the catalytic  $\text{CO}_2$  reduction. On the other hand, an equimolar mixture

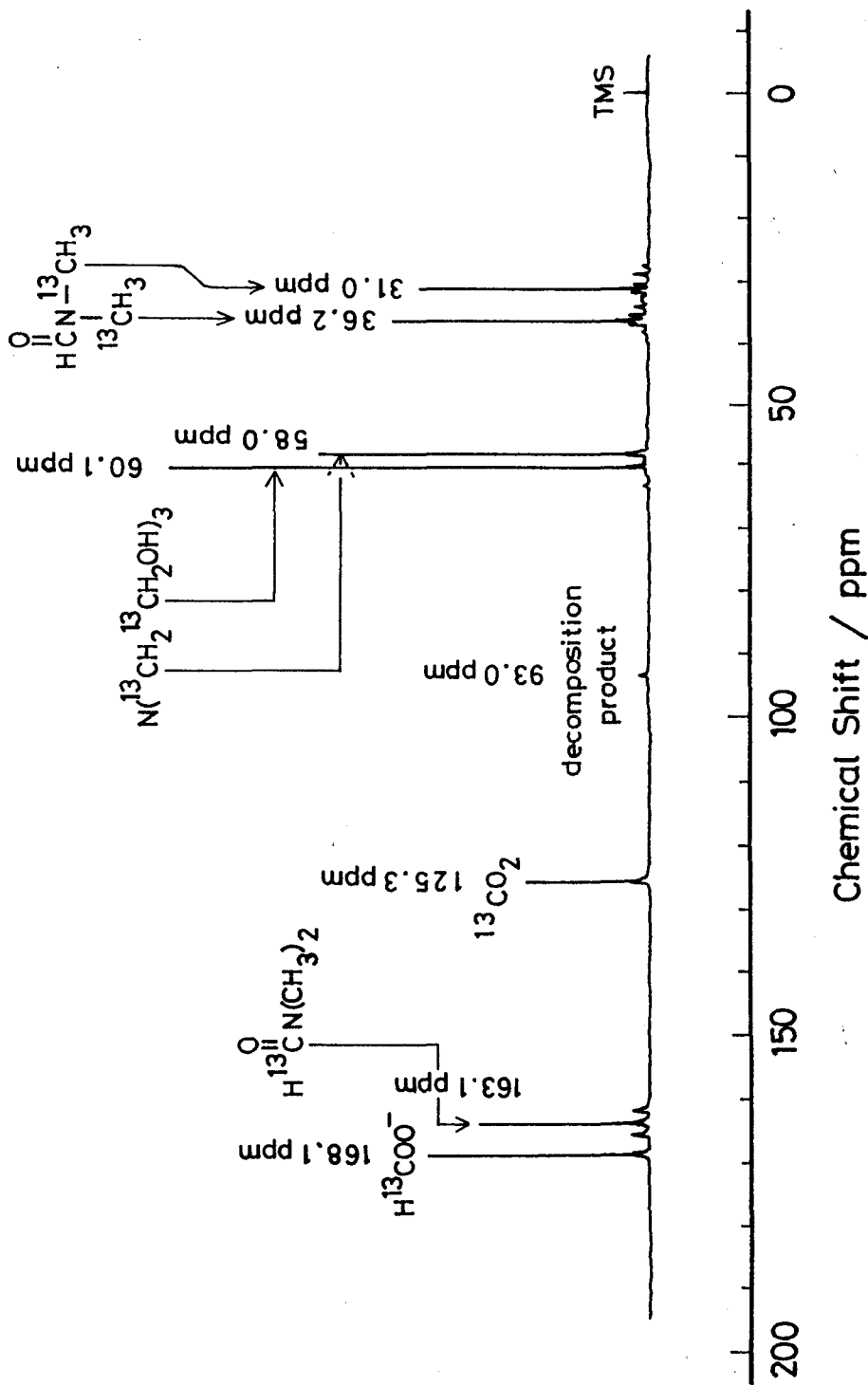


Figure 6-1.  $^{13}\text{C}$  nmr spectrum of a  $^{13}\text{CO}_2$  saturated  $\text{d}^7$ -DMF/DMF/TEOA (5:3:2 v/v) solution containing an equimolar mixture of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $5.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) after irradiation of light ( $\lambda > 320$  nm) for 20 h.

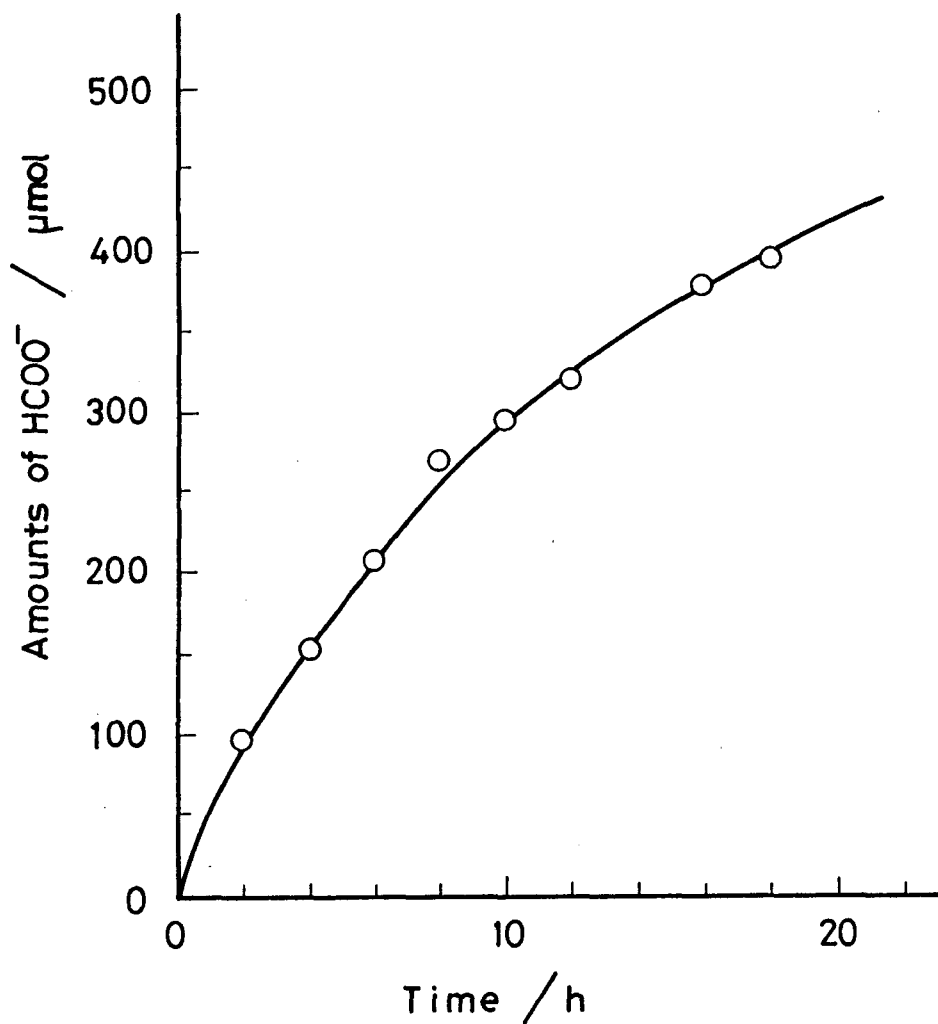


Figure 6-2. Plots of the amount of HCOO<sup>-</sup> formed vs. irradiation time in the photochemical CO<sub>2</sub> reduction in TEOA/DMF (1:4 v/v) containing an equimolar amount of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> (5.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>); λ > 320 nm.

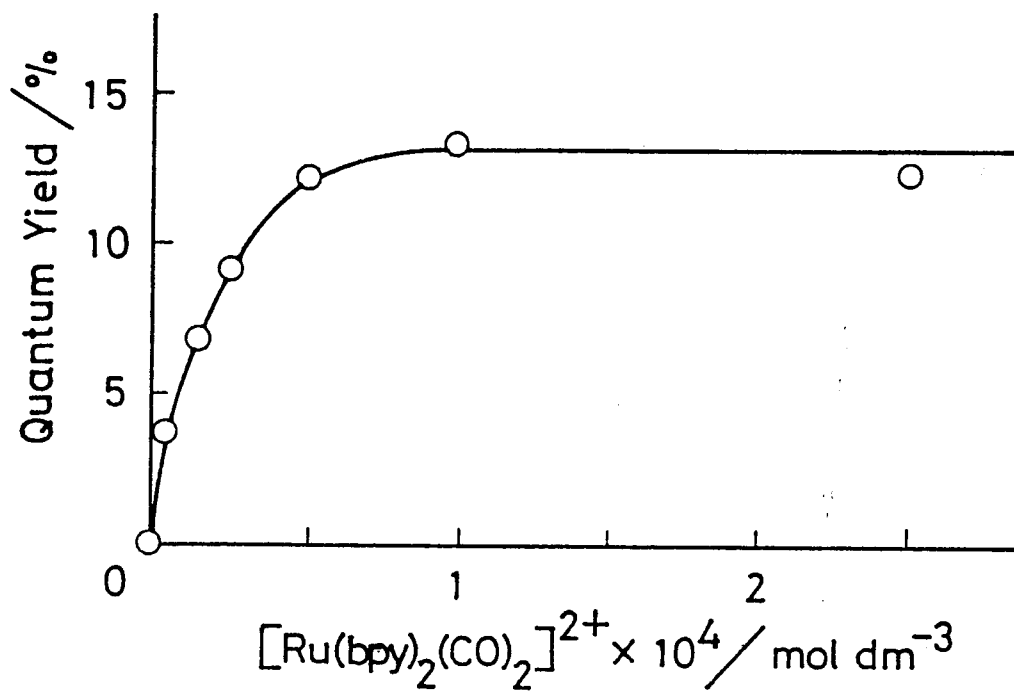


Figure 6-3. Quantum yields of the HCOO<sup>-</sup> formation at various concentrations of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>; the concentration of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> 5.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>.



of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$  gave the maximum yield for the formation of  $\text{HCOO}^-$  (entry 5 in Table 6-I). This discrepancy may be associated with a gradual decrease of catalytic activities of the  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}/\text{TEOA}$  system with time (Figure 6-2). Such a slow degradation of the catalytic activity may be caused by the decomposition of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  rather than  $[\text{Ru}(\text{bpy})_3]^{2+}$  under prolonged irradiation of light, since the electrochemical reduction of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  at more negative potentials than  $-1.0 \text{ V vs. SCE}$  in  $\text{CO}_2$ -saturated dry DMF also leads to the formation of a black precipitate, which is inactive toward both photochemical and electrochemical  $\text{CO}_2$  reductions. The concentration of TEOA also largely influences on the quantum yield for the formation of  $\text{HCOO}^-$ ; the value under constant concentrations of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) and  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) increases with increasing the concentration of TEOA up to  $2.0 \text{ mol dm}^{-3}$  to attain 16%, as shown in Figure 6-4. The maximum quantum yield thus obtained under irradiation of light ( $\lambda > 400 \text{ nm}$ ) is almost same as that in the photochemical  $\text{CO}_2$  reduction catalyzed by fac- $\text{Re}(\text{bpy})(\text{CO})_3\text{X}$  in TEOA/DMF,<sup>9</sup> where  $\text{CO}_2$  is selectively reduced to CO in contrast to the present study.

**Function of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$ .** As described in the previous sections,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  is an efficient catalyst for the electrochemical  $\text{CO}_2$  reduction under the controlled potential electrolysis conditions at  $-1.30 \text{ V vs.}$

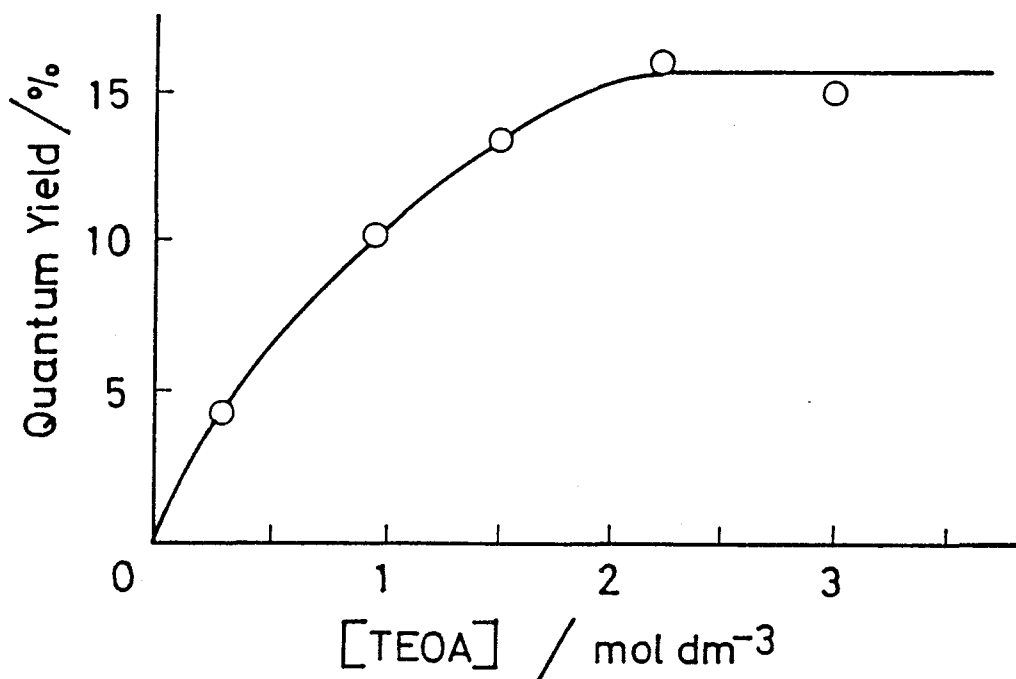
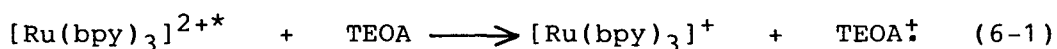


Figure 6-4. Quantum yields for the formation of  $\text{HCOO}^-$  in the photoreduction of  $\text{CO}_2$  in  $\text{CO}_2$  saturated DMF containing  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) at various concentrations of TEOA.

SCE. In contrast to  $\text{Re}(\text{bpy})(\text{CO})_3\text{X}$ , however,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  has no ability of catalyzing the photochemical  $\text{CO}_2$  reduction unless the presence of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (entry 9 in Table 6-I). This may be due to the absence of any appreciable electronic absorption band in  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in the visible region ( $\lambda > 320$  nm). In addition,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  may not be reduced by the luminescent state of  $[\text{Ru}(\text{bpy})_3]^{2+*}$ , since the luminescence from  $[\text{Ru}(\text{bpy})_3]^{2+*}$  ( $\lambda_{\text{max}}$  608 nm) has not been quenched at all by the present experimental concentrations of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  (the order of  $10^{-4}$  mol  $\text{dm}^{-3}$ ). This may be ascribed to the more negative reduction potentials of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $-0.95$  V vs. SCE) than the excited oxidation potential of  $[\text{Ru}(\text{bpy})_3]^{2+*}$  ( $-0.81$  V vs. SCE).<sup>19</sup> On the other hand, the luminescent state of  $[\text{Ru}(\text{bpy})_3]^{2+*}$  is reductively quenched by TEOA to produce  $[\text{Ru}(\text{bpy})_3]^+$  and the TEOA $^\ddagger$  radical cation with the quenching rate constant  $k_q = 1.7 \times 10^5$  mol $^{-1}$  dm $^3$  s $^{-1}$  in DMF (eq. 6-1).<sup>4a</sup> The oxidation



potential of  $[\text{Ru}(\text{bpy})_3]^+$  is  $-1.33$  V vs. SCE,<sup>19</sup> which is negative enough to reduce  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  and close to the potential applied in the electrochemical  $\text{CO}_2$  reduction catalyzed by  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ .

There has been a disagreement concerning the role of  $\text{MV}^{2+}$  as an electron relay in photochemical  $\text{CO}_2$  reductions. The irradiation of light to  $\text{CO}_2$ -saturated TEOA/DMF (1:4 v/v)

containing a high concentration of  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $1.1 \times 10^{-2} \text{ mol dm}^{-3}$ ) produced  $997 \mu\text{mol}$  of  $\text{HCOO}^-$  even in the absence of  $\text{MV}^{2+}$ , suggesting that  $\text{MV}^{2+}$  is not an essential component in the photochemical  $\text{CO}_2$  reduction in DMF. On the other hand, similar photochemical  $\text{CO}_2$  reductions using a low concentration of  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) yielded as low as  $7 \mu\text{mol}$  of  $\text{HCOO}^-$ . Such a marked difference between the amounts of  $\text{HCOO}^-$  formed in those reactions may be explained in terms of photo-assisted bipyridine (bpy) ligand dissociation from the coordinatively saturated complex  $[\text{Ru}(\text{bpy})_3]^{2+}$  affording a bis(bpy)ruthenium complex, which catalyzes the reduction of  $\text{CO}_2$ . In accordance with this, the photoirradiation ( $\lambda > 400 \text{ nm}$ ) to a  $\text{CO}_2$ -saturated TEOA/DMF (1:4 v/v) solution containing equimolar amounts of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) produced  $193 \mu\text{mol}$  of  $\text{HCOO}^-$  for 20 h. The minor activity of  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  compared with  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  as a catalyst for the reduction of  $\text{CO}_2$  (entry 5 in Table 6-I) was observed also in the electrochemical  $\text{CO}_2$  reduction catalyzed by those complexes in  $\text{H}_2\text{O}/\text{DMF}$ . This may be associated with the reduction potential of  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  ( $E_{1/2} = -1.61 \text{ V vs. SCE}$ )<sup>20</sup> being fairly negative compared with that of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $E_{\text{red}} = -0.95 \text{ V vs. SCE}$ ).

The preceding discussion suggests that the actual species for the reduction of  $\text{CO}_2$  is generated by the photo-assisted ligand dissociation from  $[\text{Ru}(\text{bpy})_3]^{2+}$ . In connection with this,  $[\text{Ru}(\text{phen})_3]^{2+}$  may be more suitable than  $[\text{Ru}(\text{bpy})_3]^{2+}$  as a photosensitizer. Thus, the photochemical  $\text{CO}_2$  reduction in  $\text{CO}_2$ -

saturated TEOA/DMF (1:4 v/v) containing  $[\text{Ru}(\text{phen})_3]^{2+}$ , in place of  $[\text{Ru}(\text{bpy})_3]^{2+}$ , and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ . The result is summarized in Table 6-II, which reveals the formation of a small amount of  $\text{HCOO}^-$  (5  $\mu\text{mol}$ ) in the absence of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  (entry 1 in Table 6-II). Coexistence of  $[\text{Ru}(\text{phen})_3]^{2+}$  and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ , however, results in a remarkable increase of the amount of  $\text{HCOO}^-$  produced (entry 2 - 7 in Table 6-II). The dependence of the amount of  $\text{HCOO}^-$  formed on the concentration of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in the presence of a fixed concentration of  $[\text{Ru}(\text{phen})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) is similar to that in the  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}$  system (compare entry 2 - 8 in Table 6-I with entry 2 - 7 in Table 6-II). The weak catalytic activity of  $[\text{Ru}(\text{phen})_3]^{2+}$  used as a photosensitizer compared with  $[\text{Ru}(\text{bpy})_3]^{2+}$  may be due to no efficient formation of  $[\text{Ru}(\text{phen})_2(\text{CO})_2]^{2+}$  by photo-assisted decomposition of  $[\text{Ru}(\text{phen})_3]^{2+}$ . This is compatible with the catalytic activity of  $[\text{Ru}(\text{phen})_2(\text{CO})_2]^{2+}$  toward the reduction of  $\text{CO}_2$ , as confirmed from the experiment that the irradiation of light to a  $\text{CO}_2$ -saturated TEOA/ $\text{CH}_3\text{CN}$  (1:4 v/v) solution containing  $[\text{Ru}(\text{phen})_2(\text{CO})_2]^{2+}$  ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) and  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) produced 73  $\mu\text{mol}$  of  $\text{HCOO}^-$  for 20 h. Thus,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  functions as an actual catalyst and  $[\text{Ru}(\text{bpy})_3]^{2+}$  plays only a role of photosensitizer in the photochemical  $\text{CO}_2$  reduction. The catalytic ability of the present system, therefore, can be evaluated in terms of a turnover number for the formation of  $\text{HCOO}^-$ , based on the amount of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ .<sup>21</sup> The maximum value has attained 3580

**Table 6-II.** Photochemical CO<sub>2</sub> reductions in CO<sub>2</sub>-saturated TEOA/DMF (1:4 v/v, 5 cm<sup>3</sup>) containing [Ru(phen)<sub>3</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> under the irradiation of light ( $\lambda > 320$  nm)<sup>a</sup> for 20 h

Entry	Concentration / mol dm <sup>-3</sup>		HCOO <sup>-</sup> / $\mu$ mol
	[Ru(phen) <sub>3</sub> ] <sup>2+</sup>	[Ru(bpy) <sub>2</sub> (CO) <sub>2</sub> ] <sup>2+</sup>	
1	5.0 x 10 <sup>-4</sup>	0	5
2	5.0 x 10 <sup>-4</sup>	2.5 x 10 <sup>-4</sup>	117
3	5.0 x 10 <sup>-4</sup>	5.0 x 10 <sup>-4</sup>	139
4	5.0 x 10 <sup>-4</sup>	7.5 x 10 <sup>-4</sup>	150
5	5.0 x 10 <sup>-4</sup>	1.0 x 10 <sup>-3</sup>	118
6	5.0 x 10 <sup>-4</sup>	1.5 x 10 <sup>-3</sup>	114
7	5.0 x 10 <sup>-4</sup>	2.0 x 10 <sup>-3</sup>	89

<sup>a</sup> 300 W-Hg lamp.

(entry 2 in Table 6-I). Even when the turnover number was calculated based on the total mole of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$ , the value is 105 (entry 4 in Table 6-I), which is still fairly larger than the value (27) in the photochemical  $\text{CO}_2$  reduction conducted in the presence of a high concentration of  $[\text{Ru}(\text{bpy})_3]^{2+}$ , reported by Lehn et al.<sup>3</sup> The detail of mechanisms of the present photochemical  $\text{CO}_2$  reductions will be described in the next chapter.

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## Chapter 7

### Photochemical CO<sub>2</sub> Reduction with an NADH Model Compound, Catalyzed by Ruthenium Complexes

#### 7-1 Introduction

All living things on earth depend for their existence on the photosynthesis and the CO<sub>2</sub> fixation using solar energy.<sup>1</sup> In the natural photosynthesis, nicotinamide adenine dinucleotide phosphate (NADP<sup>+</sup>) is reduced by H<sub>2</sub>O to afford NADPH and O<sub>2</sub>, the former of which functions as an electron donor in the CO<sub>2</sub> fixation.<sup>2</sup> NAD(P)H is a coenzyme which acts as reductants in biological redox systems, and many investigations on the model reactions of NAD(P)H have been reported.<sup>3</sup> However, there is no report on the CO<sub>2</sub> fixation with NAD(P)H model compounds.

On the other hand, there have been several papers reporting that the photochemical CO<sub>2</sub> reduction catalyzed by ruthenium complexes yields carbon monoxide as a main product.<sup>4</sup> This chapter describes the photochemical CO<sub>2</sub> reduction with an NAD(P)H model, 1-benzyl-1,4-dihydronicotinamide (BNAH) as an electron donor, catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>.

#### 7-2 Experimental Section

**Material.** BNAH prepared according to the literature<sup>5</sup> was purified by recrystallization from ethanol, and stored under N<sub>2</sub> in a refrigerator.

**Photochemical CO<sub>2</sub> Reduction with BNAH.** The manipulation for the CO<sub>2</sub> reduction was essentially the same as that described in Chapter 6; DMF or H<sub>2</sub>O/DMF was used as a reaction solvent, and an aqueous NaNO<sub>2</sub> solution (0.50 mol dm<sup>-3</sup>) was used as a cut-off chemical filter (1 cm;  $\lambda > 400$  nm). A DMF or H<sub>2</sub>O/DMF solution of ruthenium complexes was bubbled with CO<sub>2</sub> for 30 min, followed by the addition of BNAH. The resulting solution was bubbled with CO<sub>2</sub> for further 5 min. Quantum yields were determined by the method as described in Chapter 6.

Oxidation products of BNAH were determined by HPLC, <sup>1</sup>H nmr, and electronic spectra. HPLC was carried out with JASCO 880-PU equipped with a 20 cm column filled with JASCO Finepack SIL C18 using CH<sub>3</sub>OH/H<sub>2</sub>O (3:2 v/v) as an eluent, and monitored at 355 nm by JASCO 875-UV spectrophotometer. <sup>1</sup>H nmr spectra were recorded on a JEOL-PS-100 spectrometer. Electronic absorption spectra were measured with a Union SM-401 spectrophotometer.

**Quenching experiment of the luminescence state of [Ru-(bpy)<sub>3</sub>]<sup>2+\*</sup>.** The relative emission intensities at 610 nm of [Ru(bpy)<sub>3</sub>]<sup>2+\*</sup> were determined under irradiation of light at 550 nm to an N<sub>2</sub>-saturated DMF solution of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (2.5 x 10<sup>-4</sup> mol dm<sup>-3</sup>) in the presence of various amounts of BNAH as a

quencher with a Hitachi 650-10S Fluorescence Spectrophotometer. The Stern-Volmer relationship (eq. 7-1) was obtained between the

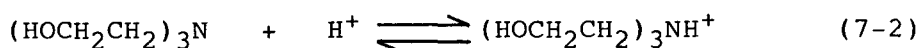
$$I_0/I = 1 + k_q\tau[Q] \quad (7-1)$$

concentration of the quencher (Q) and the relative emission intensity ( $I_0/I$ ), where  $I_0$  and  $I$  represent the intensity at 610 nm in the absence ( $I_0$ ) and the presence of a quencher ( $I$ ), respectively. The quenching rate constant  $k_q$  ( $= K_q\tau^{-1}$ ) was determined from the Stern-Volmer constant  $K_q$  and the emission lifetime  $\tau$  ( $[\text{Ru}(\text{bpy})_3]^{2+}$  930 ns in DMF).<sup>6</sup>

### 7-3 Results and Discussion

**Photochemical  $\text{CO}_2$  Reduction by using BNAH as an Electron Donor.** As mentioned in the preceding chapter, triethanolamine is an efficient electron donor in the photochemical  $\text{CO}_2$  reduction catalyzed by  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ . On the other hand,  $\text{H}_2\text{O}$  may largely influence on the photochemical  $\text{CO}_2$  reduction; the catalytic system composed of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $1.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) and  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) afforded  $\text{HCOO}^-$  (315  $\mu\text{mol}$ ) in  $\text{CO}_2$ -saturated TEOA/DMF (1:4 v/v) for 20 h as described in Chapter 6, whereas the amount of  $\text{HCOO}^-$  decreased (209  $\mu\text{mol}$ ) and no carbon monoxide generated in the  $\text{CO}_2$  reduction conducted in  $\text{H}_2\text{O}/\text{TEOA}/\text{DMF}$  (1:2:7 v/v) otherwise the same conditions. The decrease in the amount of  $\text{HCOO}^-$  produced in the

latter may arise from the decreasing electron donor ability of TEOA due to the protonation to TEOA ( $pK_a = 7.9$ ) in protic conditions (eq. 7-2).<sup>7</sup> The electrochemical  $CO_2$  reduction catalyzed by



$[Ru(bpy)_2(CO)_2]^{2+}$  produced CO and  $HCOO^-$ , whose relative amounts depend on the proton concentration in the medium used. For examining such an effect of the proton concentration on the photochemical  $CO_2$  reduction, however, a strong basic electron donor such as TEOA may be improper. Photochemical  $CO_2$  reduction using BNAH as an electron donor under protic conditions is, therefore, of much interest in the viewpoint that BNAH is a model compound of NAD(P)H, which functions as an electron donor in biological photosyntheses.

Irradiation of visible light ( $\lambda > 400$  nm) to a  $CO_2$ -saturated dry DMF solution<sup>8</sup> containing  $[Ru(bpy)_2(CO)_2]^{2+}$  ( $1.0 \times 10^{-4}$  mol  $dm^{-3}$ ),  $[Ru(bpy)_3]^{2+}$  ( $5.0 \times 10^{-4}$  mol  $dm^{-3}$ ), and BNAH ( $0.10$  mol  $dm^{-3}$ ) produces trace amounts of  $HCOO^-$  and CO, as shown by a broken line in Figure 7-1, where a black precipitate occurred. On the other hand, the amounts of those reaction products are largely increased when the reduction is conducted in  $CO_2$ -saturated  $H_2O/DMF$  (1:9 v/v) (a solid line in Figure 7-1), and no appreciable black precipitate was formed in the reaction mixture. These results suggest that  $H_2O$  functions as a proton donor to depress the decomposition of  $[Ru(bpy)_2(CO)_2]^{2+}$  in the photochemical  $CO_2$

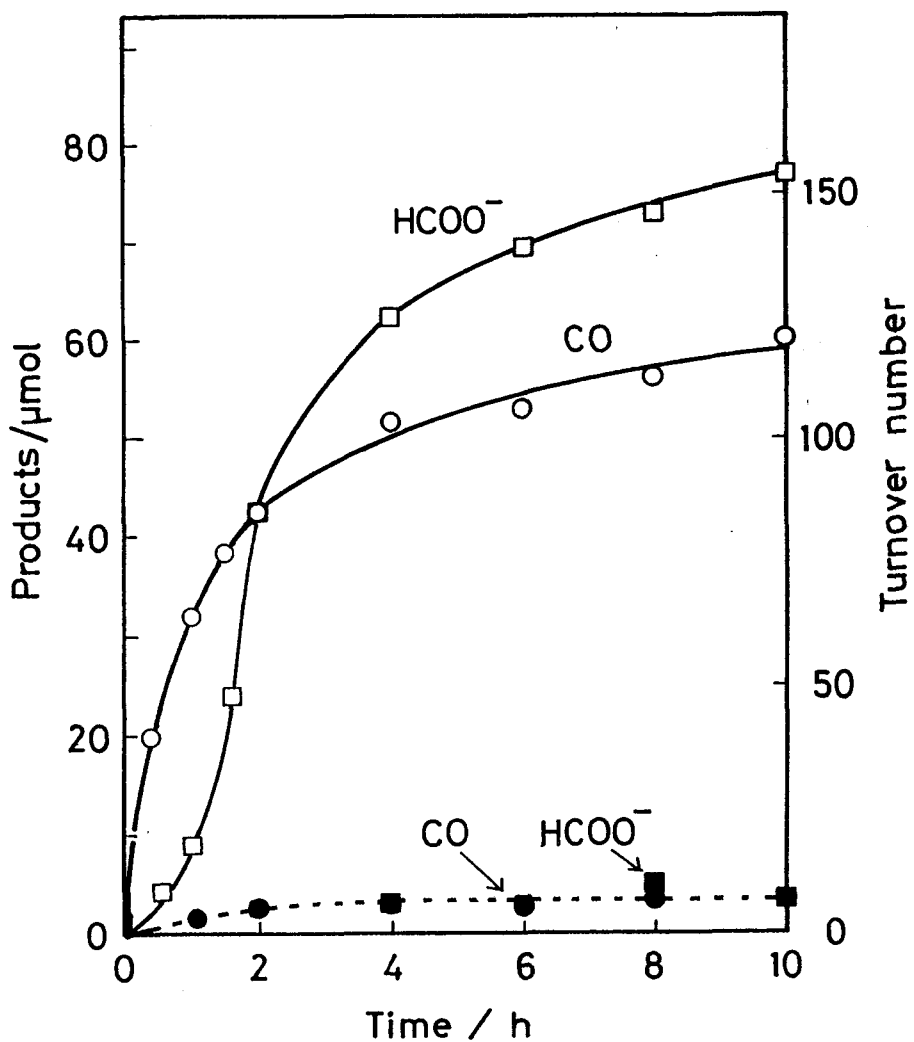


Figure 7-1. The photochemical CO<sub>2</sub> reduction with the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (5.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>)/[Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> (1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>)/BNAH (0.10 mol dm<sup>-3</sup>) system in CO<sub>2</sub>-saturated H<sub>2</sub>O/DMF (1:9 v/v) (—) and in DMF (----); λ > 400 nm.

reduction.<sup>9</sup> It should be noted that  $\text{HCOO}^-$  is selectively formed in the photochemical  $\text{CO}_2$  reduction by using TEOA as an electron donor, as described in Chapter 6, while not only  $\text{HCOO}^-$  but also CO are formed in the similar  $\text{CO}_2$  reduction when BNAH is used as an electron donor in  $\text{H}_2\text{O}/\text{DMF}$  (1:9 v/v), where the quantum yields for the formation of CO and  $\text{HCOO}^-$  in the initial stage were 14.8 and 2.7%, respectively. In the initial 2 h, CO is produced as the main product, whereas the rate of formation of CO is rapidly lowered after 2 h, and then  $\text{HCOO}^-$  becomes the main product (Figure 7-1). Such alternation of the main product in the photochemical  $\text{CO}_2$  reduction with the  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}/\text{BNAH}$  system may not be due to decomposition of the catalytic system during the irradiation of light, since the catalytic system does not lose the ability of the photochemical  $\text{CO}_2$  reduction in  $\text{H}_2\text{O}/\text{DMF}$  (3:7 v/v) even after 10 h, as depicted in Figure 7-2, which shows CO as the main product throughout the reaction. The initial rates of the formation of both CO and  $\text{HCOO}^-$  in  $\text{H}_2\text{O}/\text{DMF}$  (3:7 v/v) are, however, slower than that in  $\text{H}_2\text{O}/\text{DMF}$  (1:9 v/v), and the quantum yields for the formation of CO and  $\text{HCOO}^-$  were decreased down to 8.6 and 1.9%, respectively, in  $\text{H}_2\text{O}/\text{DMF}$  (3:7 v/v).

The function of BNAH in the photochemical  $\text{CO}_2$  reduction is essentially the same as that of TEOA, since the former is not excited by irradiation of light ( $\lambda > 400$  nm). The quenching constant ( $k_q$ ) of the luminescence state of  $[\text{Ru}(\text{bpy})_3]^{2+}$  by BNAH (eq. 7-3) is  $2.0 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  (in DMF), which is fairly

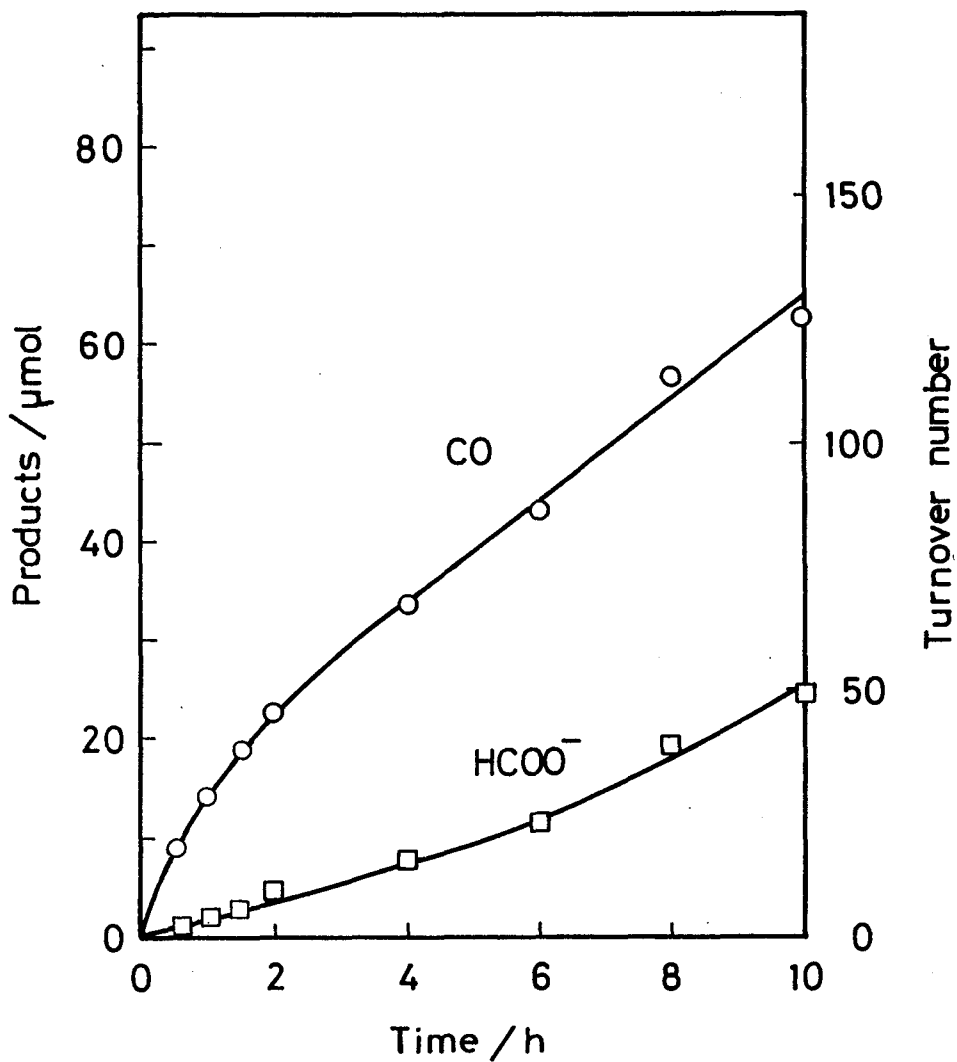


Figure 7-2. The photochemical  $\text{CO}_2$  reduction with the  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ )/ $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ )/BNAH ( $0.10 \text{ mol dm}^{-3}$ ) system in  $\text{CO}_2$ -saturated  $\text{H}_2\text{O}/\text{DMF}$  (3:7 v/v);  $\lambda > 400 \text{ nm}$ .



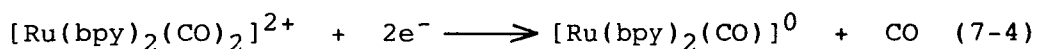


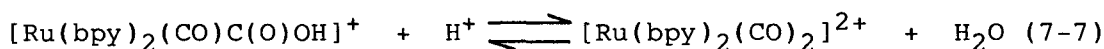
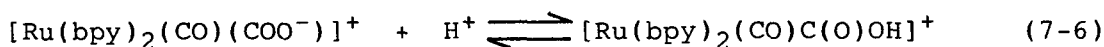
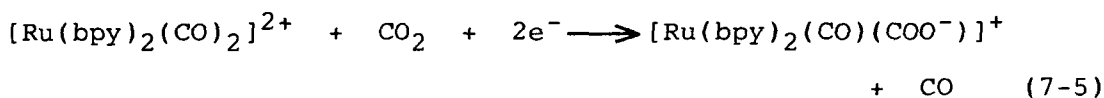
larger than that by TEOA owing to the difference of the oxidation potential of BNAH (+0.57 V vs. SCE)<sup>6</sup> and TEOA (+0.82 V vs. SCE).<sup>10</sup> Thus, BNAH is superior to TEOA as an electron donor. In accordance with this, the quantum yields for the formation of HCOO<sup>-</sup> with the [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> (1.0 x 10<sup>-4</sup> mol dm<sup>-3</sup>)/[Ru(bpy)<sub>3</sub>]<sup>2+</sup> (5.0 x 10<sup>-4</sup> mol dm<sup>-3</sup>)/TEOA (0.10 mol dm<sup>-3</sup>) system under irradiation of light (λ > 400 nm) were as low as 1 and 2% in CO<sub>2</sub>-saturated DMF and H<sub>2</sub>O/DMF (1:9 v/v), respectively. On the other hand, 4,4'- and 4,6'-linked dimer of BNAH are generated as oxidation products of BNAH in the course of the present photoreduction, suggesting that the dimerization reaction of BNAH<sup>‡</sup> generated in the photoreaction is faster than the deprotonation reaction of BNAH<sup>‡</sup>, though BNAH<sup>‡</sup> is a relatively strong acid (pK<sub>a</sub> = 3.5). This is consistent with the fact that the present reduction requires any proton donors such as water. Thus, it may be concluded that BNAH functions as an electron donor but not a proton donor.

**Mechanism of the photochemical CO<sub>2</sub> Reduction Catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in the Presence of Photosensitizer.** It has been proposed that the photochemical CO<sub>2</sub> reduction in the presence of a high concentration of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (1.1 x 10<sup>-2</sup> mol dm<sup>-3</sup>) in TEOA/DMF is initiated by ligand photodissociation of

$[\text{Ru}(\text{bpy})_3]^+$ , followed by protonation, affording a bis(bipyridine)ruthenium hydride species, which undergoes an insertion reaction by  $\text{CO}_2$  to produce a formate complex, followed by the reduction to give  $\text{HCOO}^-$ . This mechanism may, however, be argued against the following points; i) no insertion reaction of  $\text{CO}_2$  to the ruthenium hydride species has been observed, ii)  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{H}]^+$  is known to react with water to evolve  $\text{H}_2$ , though no appreciable  $\text{H}_2$  evolution was detected in the present  $\text{CO}_2$  reduction in  $\text{H}_2\text{O}/\text{DMF}$ , and iii) a formate complex such as  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{OC}(\text{O})\text{H}]^+$  may be unreasonable as a precursor for the formation of  $\text{CO}$ . On the other hand, the variation of the main product in the photochemical  $\text{CO}_2$  reduction upon changing not only the electron donor but also the content of  $\text{H}_2\text{O}$  in  $\text{DMF}$  strongly suggests that the mechanism of the photochemical  $\text{CO}_2$  reduction may be essentially the same as that of the electrochemical  $\text{CO}_2$  reduction, in which  $\text{CO}$  and  $\text{HCOO}^-$  are selectively produced by choosing the acidity of the proton source.

As described in Chapter 2,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  undergoes simultaneous irreversible two-electron reduction at  $-0.95$  V vs. SCE to liberate a single  $\text{CO}$  molecule (eq. 7-4). On the other hand, the electrochemical reduction of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  at  $-1.10$  V vs. SCE in  $\text{CO}_2$ -saturated dry  $\text{DMF}$  gives  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  (eq. 7-5), which exists as an equilibrium mixture with  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$  (eq. 7-6) and  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  (eq. 7-7) in aqueous





solutions. In view of these facts, the most plausible mechanism of the present photochemical  $\text{CO}_2$  reduction may be as follows; the luminescent state of  $[\text{Ru}(\text{bpy})_3]^{2+*}$  is reductively quenched by TEOA and BNAH to afford  $[\text{Ru}(\text{bpy})_3]^+$  together with TEOA $^\ddagger$  and BNAH $^\ddagger$ , respectively, the former of which is decomposed to hydroxyacetaldehyde and diethylamine, and the latter dimerizes to give 4,4'- and 4,6'-linked dimers.<sup>11</sup> On the other hand,  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $E_{\text{red}} = -0.95 \text{ V vs. SCE}$ ) may be reduced by two moles of  $[\text{Ru}(\text{bpy})_3]^+$  ( $E_{1/2} = -1.35 \text{ V vs. SCE}$ ) with regenerating two moles of  $[\text{Ru}(\text{bpy})_3]^{2+}$ ; the one-electron reduced species of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  may be unstable to liberate a single CO ligand, and  $[\text{Ru}(\text{bpy})_2(\text{CO})]^+$  thus formed is further reduced by  $[\text{Ru}(\text{bpy})_3]^+$  to afford a penta-coordinate complex  $[\text{Ru}(\text{bpy})_2(\text{CO})]^0$  (eq. 7-4), which reacts with  $\text{CO}_2$  to afford a hexa-coordinate  $\text{CO}_2$  adduct  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$  (eq. 7-5). The equilibrium constants of eqs. 7-6 and 7-7, therefore, may explain the reaction products in the present study. Thus, the formation of CO in  $\text{H}_2\text{O}/\text{DMF}$  (1:9 and 3:7 v/v) may be due to the two electron reduction of  $[\text{Ru}(\text{bpy})_2]^{2+}$ .

$(\text{CO})_2]^{2+}$  (eq. 7-4) generated by the protonation to  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{-C}(\text{O})\text{OH}]^+$  (eq. 7-7) in  $\text{H}_2\text{O}/\text{DMF}$ , and the selective formation of  $\text{HCOO}^-$  in  $\text{CO}_2$ -saturated  $\text{TEOA}/\text{DMF}$  may be resulted from the irreversible two-electron reduction of either  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{-}(\text{COO}^-)]^+$  or  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$  <sup>12</sup> with two moles of  $[\text{Ru}(\text{bpy})_3]^+$ . Such alternation of the main product from  $\text{CO}$  to  $\text{HCOO}^-$  in the photochemical  $\text{CO}_2$  reduction in  $\text{H}_2\text{O}/\text{DMF}$  (1:9 v/v) may be associated with the shift of the equilibrium of eq. 7-7 to the left owing to the consumption of protons accompanied with the reduction. In accordance with this, the electrochemical  $\text{CO}_2$  reduction catalyzed by  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in  $\text{H}_2\text{O}/\text{DMF}$  (1:9 v/v) affords  $\text{CO}$  at pH 6.0, and a mixture of  $\text{CO}$  and  $\text{HCOO}^-$  at pH 9.0 (Chapter 2). Furthermore, the selective formation of  $\text{HCOO}^-$  has been achieved not only in the photochemical  $\text{CO}_2$  reduction in  $\text{TEOA}/\text{DMF}$  but also in the electrochemical  $\text{CO}_2$  reduction in dry- $\text{CH}_3\text{CN}$  containing  $(\text{CH}_3)_2\text{NH}_2^+$  or  $\text{C}_6\text{H}_5\text{OH}$  as a proton source, as described in Chapter 3.

#### 7-4 References

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- (8) The DMF solution of  $[\text{Ru}(\text{bpy})_3]^{2+}$  contains a small amount of  $\text{H}_2\text{O}$  arising from  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ .
- (9) The black precipitate has no catalytic activity for the reduction of  $\text{CO}_2$ , since the addition of water to the reaction mixture obtained after irradiation of visible light to the  $\text{CO}_2$ -saturated dry DMF containing  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ),  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ), and BNAH ( $0.10 \text{ mol dm}^{-3}$ ) for 5 h resulted

in no appreciable increase of either  $\text{HCOO}^-$  or CO compared with the result shown by a dotted line in Figure 7-1.

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## Conclusion

The results obtained from the present investigation are summarized as follow.

Chapter 1: The water gas shift reaction (WGSR) catalyzed by bis(2,2'-bipyridine) carbonyl ruthenium(II) complexes under mild conditions (70 - 150°C; 3 - 20 kg cm<sup>-2</sup> of CO) has been investigated. Turnover numbers for the H<sub>2</sub> formation of about 500 in 20 h have been obtained in an aqueous KOH solution containing [Ru(bpy)<sub>2</sub>(CO)Cl](PF<sub>6</sub>) (bpy = 2,2'-bipyridine) as a catalyst precursor. The solvolysis of [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup> in an aqueous solution affords [Ru(bpy)<sub>2</sub>(CO)(H<sub>2</sub>O)]<sup>2+</sup>, which exists as an equilibrium mixture with [Ru(bpy)<sub>2</sub>(CO)(OH)]<sup>+</sup> in weak alkaline solutions. A water molecule ligated to [Ru(bpy)<sub>2</sub>(CO)(H<sub>2</sub>O)]<sup>2+</sup> is readily substituted by CO under CO pressures to produce [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>, which undergoes a nucleophilic attack of OH<sup>-</sup> to afford [Ru(bpy)<sub>2</sub>(CO)C(O)OH]<sup>+</sup>. The hydroxycarbonyl complex not only exists as an equilibrium mixture with [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> and [Ru(bpy)<sub>2</sub>(CO)(COO<sup>-</sup>)]<sup>+</sup> in alkaline media but also undergoes a decarboxylation reaction at elevated temperatures to give CO<sub>2</sub> and [Ru(bpy)<sub>2</sub>(CO)H]<sup>+</sup>, the latter of which further reacts with H<sub>3</sub>O<sup>+</sup> to evolve H<sub>2</sub>, regenerating [Ru(bpy)<sub>2</sub>(CO)(H<sub>2</sub>O)]<sup>2+</sup>. All these species involved in the cycle of the WGS reaction catalyzed by [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup> have been isolated or characterized by spectrophotometry.

Chapter 2: The controlled potential electrolysis of CO<sub>2</sub>-

saturated H<sub>2</sub>O (pH 6.0)/DMF (9:1 v/v) solutions containing [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> or [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup> at -1.50 V vs. SCE catalytically produces CO together with H<sub>2</sub>. The same electrolysis of a CO<sub>2</sub>-saturated alkaline solution, H<sub>2</sub>O (pH 9.5)/DMF (9:1 v/v), gives not only CO and H<sub>2</sub> but also HCOO<sup>-</sup>. The effect of pH on the formation of CO and HCOO<sup>-</sup> in the reduction of CO<sub>2</sub> is explained in terms of the generation of an unstable penta-coordinated Ru(0) complex [Ru(bpy)<sub>2</sub>(CO)]<sup>0</sup> as an intermediate in the irreversible two-electron reduction of [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> or [Ru(bpy)<sub>2</sub>(CO)Cl]<sup>+</sup>; the Ru(0) intermediate is added with CO<sub>2</sub> to afford [Ru(bpy)<sub>2</sub>(CO)-(COO<sup>-</sup>)]<sup>+</sup>, which reacts with protons to produce [Ru(bpy)<sub>2</sub>(CO)-C(O)OH]<sup>+</sup> in weak alkaline conditions. The resulting [Ru(bpy)<sub>2</sub>(CO)C(O)OH]<sup>+</sup> is further converted to [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> by dehydroxyration in acidic conditions. The [Ru(bpy)<sub>2</sub>(CO)C(O)OH]<sup>+</sup> and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> complexes thus produced undergo two-electron reduction to afford HCOO<sup>-</sup> and CO, respectively, with regenerating [Ru(bpy)<sub>2</sub>(CO)]<sup>0</sup>.

Chapter 3: The selectivity for the formation of HCOO<sup>-</sup> in the electrochemical CO<sub>2</sub> reduction catalyzed by [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> in CH<sub>3</sub>CN is drastically dependent on the acidity of proton sources used. The selectivity increases with decreasing the acidity of proton sources, and almost selective formation of HCOO<sup>-</sup> is achieved by using (CH<sub>3</sub>)<sub>2</sub>NH·HCl or C<sub>6</sub>H<sub>5</sub>OH as a proton source in CH<sub>3</sub>CN. The selective HCOO<sup>-</sup> formation may be explained by the fact that the conversion from [Ru(bpy)<sub>2</sub>(CO)C(O)OH]<sup>+</sup> to [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup> does not occur with such proton sources of low



acidities.

Chapter 4:  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$  and  $\text{RuL}_3(\text{CO})_2\text{Cl}_2$  ( $\text{L}_1, \text{L}_2 = 2,2'$ -bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), and 1,10-phenanthroline (phen);  $\text{L}_3 = \text{bpy}$  and dmbpy) were synthesized, and the catalytic activity and the product distribution in the electrochemical  $\text{CO}_2$  reductions were examined. The equilibria among  $[\text{RuL}_1\text{L}_2(\text{CO})_2]^{2+}$ ,  $[\text{RuL}_1\text{L}_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$  and  $[\text{RuL}_1\text{L}_2(\text{CO})\text{-(COO}^-)]^+$  are shifted to the former with substitution of a dmbpy ligand to bpy of the catalyst, and the CO generation in the electrochemical  $\text{CO}_2$  reductions becomes more predominant. This may be due to a donor property of dmbpy stronger than the bpy ligand.  $[\text{Ru}(\text{phen})_2(\text{CO})_2]^{2+}$  exhibits a weak catalytic activity compared with  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  though these complexes were almost same in the electrochemical properties.

Chapter 5: Electrochemical  $\text{CO}_2$  reduction catalyzed by  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  in the presence both of  $(\text{CH}_3)_2\text{NH}$  and of  $(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$  in anhydrous  $\text{CH}_3\text{CN}$  catalytically produces  $\text{HCOO}^-$  and N,N-dimethylformamide (DMF) with current efficiency 75.7 and 21.4%, respectively. The formation of the carbamoyl complex,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{N}(\text{CH}_3)_2]^+$ , as an intermediate for the DMF generation was confirmed by FT-IR and  $^1\text{H}$  nmr spectra.

Chapter 6: A catalytic system composed of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  /  $[\text{Ru}(\text{bpy})_3]^{2+}$  or  $[\text{Ru}(\text{phen})_3]^{2+}$  / triethanolamine (TEOA) selectively produces  $\text{HCOO}^-$  from  $\text{CO}_2$ -saturated N,N-dimethylformamide (DMF) and  $\text{CH}_3\text{CN}$  under irradiation of light ( $\lambda > 320$  or 400 nm), where  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ,  $[\text{Ru}(\text{bpy})_3]^{2+}$  or  $[\text{Ru}(\text{phen})_3]^{2+}$ , and TEOA function

as a catalyst, a photosensitizer, and an electron donor, respectively. The maximum quantum yield for the formation of  $\text{HCOO}^-$  attains 16% in the system composed of  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$  ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ),  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) and TEOA ( $2.0 \text{ mol dm}^{-3}$ ).

Chapter 7: The photochemical  $\text{CO}_2$  reduction conducted in  $\text{H}_2\text{O}/\text{DMF}$  (1:9 and 3:7 v/v) using 1-benzyl-1,4-dihydronicotinamide (BNAH) as an electron donor in place of TEOA affords CO as a main product together with  $\text{HCOO}^-$ . Quantum yields for the formation of CO and  $\text{HCOO}^-$  achieve 14.8 and 2.7%, respectively, in  $\text{H}_2\text{O}/\text{DMF}$  (1:9 v/v). The predominance of CO to  $\text{HCOO}^-$  formed in  $\text{H}_2\text{O}/\text{DMF}$  (3:7 v/v) is higher than that in  $\text{H}_2\text{O}/\text{DMF}$  (1:9 v/v). Not only the alternation of the main product from  $\text{HCOO}^-$  to CO upon using BNAH as an electron donor in place of TEOA but also the predominant formation of CO to  $\text{HCOO}^-$  with increasing the  $\text{H}_2\text{O}$  content in DMF may be explained in terms of the acid-base equilibria among  $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ ,  $[\text{Ru}(\text{bpy})_2(\text{CO})\text{C}(\text{O})\text{OH}]^+$ , and  $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COO}^-)]^+$ , which may participate as actual catalysts in the catalytic cycle of the photochemical  $\text{CO}_2$  reduction. The present reaction system is the first example for the  $\text{CO}_2$  reduction with a model compound of NAD(P)H which is an electron donor in the photosynthetic systems.

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