Electrochemical CO₂ Reduction Catalyzed by [Ru(bpy)₂(CO)₂]²⁺ and [Ru(bpy)₂(CO)Cl]⁺. The Effect of pH on the Formation of CO and HCOO⁻

Hitoshi Ishida, Koji Tanaka, and Toshio Tanaka

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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The controlled potential electrolysis of CO₂-saturated H₂O (pH 6.0)/DMF (9:1, v/v) solution containing [Ru(bpy)₂(CO)₂]²⁺ or [Ru(bpy)₂(CO)Cl]⁺ at -1.50 V vs. SCE catalytically produces CO together with H₂. The same electrolysis of a CO₂-saturated alkaline solution, H₂O (pH 9.5)/DMF (9:1, v/v), gives not only CO and H₂ but also HCOO⁻. The effect of pH on the formation of CO and HCOO⁻ in the reduction of CO₂ is explained in terms of the generation of unstable pentacoordinated Ru(0) complex [Ru(bpy)₂(CO)]⁰ as an intermediate in the irreversible two-electron reduction of [Ru(bpy)₂(CO)₂]²⁺ or [Ru(bpy)₂(CO)Cl]⁺; the Ru(0) intermediate is added by CO₂ to afford [Ru(bpy)₂(CO)(CO₂)]⁺, which reacts with protons to produce [Ru(bpy)₂(CO)(CO₂)OH]⁺ in weak alkaline conditions. The resulting [Ru(bpy)₂(CO)(CO₂)OH]⁺ is further converted to [Ru(bpy)₂(CO)(CO₂)₂]²⁻ by dehydroxylation in acidic conditions. The [Ru(bpy)₂(CO)₂(CO₂)(O)OH]⁺ and [Ru(bpy)₂(CO)₂(CO₂)(O)OH]⁺ complexes thus produced undergo two-electron reduction to afford HCOO⁻ and CO, respectively, with regeneration of [Ru(bpy)₂(CO)]⁰.

Introduction

Effective utilization of CO₂ being an ultimate oxidation product of organic molecules is one of the most important subjects in the field of chemistry to cope with a predictable oil shortage in the near future. Along this line, electrochemical,¹⁻¹⁰ photochemical,¹¹⁻¹⁸ and thermal¹⁹⁻²¹ reductions of CO₂ have been studied by using homogeneous catalysts. Of these, the electrochemical reduction of CO₂ seems to have a bright prospect compared with other methods, since the reaction can easily be controlled by changing the applied potentials.

Electrochemical reduction of CO₂ giving CO₂⁻ requires more negative potentials than -2.10 V vs. SCE (eq 1).¹⁰

\[
\text{CO}_2 + e^- \rightarrow \text{CO}_2^- \quad (E_0 = -2.10 \text{ V})
\] (1)

However, CO₂ 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 and 3, respectively) are -0.85 and -0.76 V vs. SCE, respectively, in water at pH 7.0.¹¹ These values are somewhat more negative than the redox potential of the H₂/H₂⁺ couple at pH 7.0 (eq 4).¹¹ In order to depress

\[
\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH} \quad (E_0 = -0.85 \text{ V})
\] (2)

\[
\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2 \quad (E_0 = -0.76 \text{ V})
\] (3)

the evolution of H₂ in the course of reduction of CO₂, therefore, it is desirable to use any catalysts which have a strong affinity for CO₂ even in the presence of protons. Of a number of transition-metal complexes as catalysts for the reduction of CO₂, rhodium and ruthenium complexes have especially been of much interest from the viewpoint of efficiency of formation of CO, HCOO⁻, or both.¹⁻⁴

Recently, we have reported that one of the carbonyl groups of [Ru(bpy)₂(CO)]²⁺ (bpy = 2,2'-bipyridine) undergoes a nucleophilic attack of OH⁻ in a weak alkaline aqueous solution to afford [Ru(bpy)₂(CO)(CO)(OH)]⁺ (eq 5), which further reacts with OH⁻ at pH > 9 to give a deprotonated species, [Ru(bpy)₂(CO)(CO)OH]⁺ (eq 6).²²

\[
\text{[Ru(bpy)₂(CO)]²⁺} + \text{OH}^- \rightarrow \text{[Ru(bpy)₂(CO)(CO)(OH)]⁺} \quad \text{(5)}
\]

\[
\text{[Ru(bpy)₂(CO)(CO)(OH)]⁺} + \text{OH}^- \rightarrow \text{[Ru(bpy)₂(CO)(CO)OH]⁺} + \text{H}_2\text{O} \quad \text{(6)}
\]
unstable owing to the apparent 20-electron configuration around the central ruthenium atom. For the same reason, the two-electron reduction product of \([\text{Ru(bpy)}_2(\text{CO})_2]^2\) may be unstable to liberate one molecule of CO. Pentacoordinated Ru(0) thus formed may be oxidized by CO₂ and stabilized to generate \([\text{Ru(bpy)}_2(\text{CO})(\text{COO})]^+\), which may be converted to \([\text{Ru(bpy)}_2(\text{CO})]^+\) in acidic conditions.

We have also found that the formation of CO and HCOO⁻ is largely influenced by proton concentrations in the electrochemical reduction of CO₂ catalyzed by \([\text{Ru(bpy)}_2(\text{CO})_2]^2\). This paper reports the catalytic cycle involving \([\text{Ru(bpy)}_2(\text{CO})]^+\), \([\text{Ru(bpy)}_2(\text{CO})(\text{COO})]^+\), and \([\text{Ru(bpy)}_2(\text{CO})(\text{COO})^-]\) as intermediates or active species to generate CO and HCOO⁻ in the electrochemical reduction of CO₂.

**Experimental Section**

**Materials.** \(\text{Ru(bpy)}_2\text{Cl}_2\cdot \text{H}_2\text{O}\), \([\text{Ru(bpy)}_2(\text{CO})\text{Cl}](\text{PF}_6)\), and \([\text{Ru(bpy)}_2(\text{CO})_2](\text{PF}_6)\) were prepared according to the literature. Commercially available guaranteed reagent grades of LiCl, NaOH, \(\text{H}_2\text{PO}_4\), \(\text{NaHCO}_3\), \(\text{Na}_{2}\text{CO}_3\), and \(n\)-Bu\text{NH}_2 were used without further purification. \(n\)-Bu\text{NClO}_4 prepared by the reaction of \(n\)-Bu\text{NBr} with \(\text{HClO}_4\) 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 NaBH₄ successively and then distilled under reduced pressure.

**Physical Measurements.** Electrochemical measurements were carried out in a Pyrex cell (30 or 100 cm³) 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 \(\text{N}_2\) or \(\text{CO}_2\) at atmospheric pressure. 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 ± 0.07 mm² 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), 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).

**Electrochemical Reduction of \(\text{CO}_2\).** The reduction of \(\text{CO}_2\) in a \(\text{CO}_2\)-saturated \(\text{H}_2\text{O}/\text{DMF}\) mixture containing \([\text{Ru(bpy)}_2(\text{CO})_2]\) or \([\text{Ru(bpy)}_2(\text{CO})]\) was carried out by the controlled potential electrolysis at \(-1.50 \text{ V vs. SCE}\) on an Hg electrode. The electrolysis cell consisted of three compartments (Figure 1): one for an Hg working electrode (3.1 cm²), the second, separated from the working electrode cell by a glass frit, for a platinum auxiliary electrode (ca. 3 cm²), and the third for an SCE reference electrode. The volume of these compartments was 35, 25, and 8 cm³, respectively, and the former two connected to volumetric flasks with stainless steel tubes (i.d. = 0.4 mm). \(\text{CO}_2\)-saturated \(\text{H}_2\text{O}/\text{DMF}\) solutions containing \([\text{Ru(bpy)}_2(\text{CO})_2]\) or \([\text{Ru(bpy)}_2(\text{CO})]\) (0.50 mmol dm⁻³) were prepared by mixing a \(\text{CO}_2\)-saturated DMF solution containing either the Ru(I) complex (0.025 mmol, 5–45 cm³) with \(\text{CO}_2\)-saturated water (pH 6.0 or 9.5, 5–45 cm³) and \(\text{H}_2\text{PO}_4\) and \(\text{NaBH}_4\), successively and then distilled under \(\text{N}_2\) atmosphere. N,N-Dimethylformamide (DMF) 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 303 ± 0.1 K, and the solution was stirred magnetically for 1 h. Attainment of the thermal equilibrium of \(\text{CO}_2\) between the gaseous and liquid phases in the cell was confirmed from a constant height of the meniscus of \(\text{CO}_2\)-saturated water in the volumetric flasks connected to 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 coulombmeter.

**Product Analysis.** At a fixed interval of coulombs consumed in the reduction, each 0.1-cm³ portion of gas was sampled from the gaseous phases of both the working electrode compartment and the volumetric flask with a pressure-locked syringe (Precision Sampling). Gaseous products were analyzed on a Shimadzu GC-7BT gas chromatograph equipped with a 2-m column filled with Molecular Sieve 13X using He as a carrier gas (for the determination of \(\text{CO}_2\)) and on a Shimadzu GC-7A gas chromatograph equipped with a 2-m column filled with Unibeads 1S using \(N_2\) 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 to the working electrode compartment. The analysis of the solution was performed by sampling each 0.1-cm³ portion from the working electrode compartment through a septum cap by syringe technique at a fixed interval of coulombs consumed. The amount of HCOO⁻ produced in the solution was determined with a Shimadzu Isotachphoretic Analyzer IP-2A using aqueous \(\text{Cd(NO}_3)_2\) (6.0 mmol dm⁻³) and caprylic acid (10.0 mmol dm⁻³) solutions as leading and terminal electrolytes, respectively.

**Results and Discussion**

**Cyclic Voltammetry of the Ruthenium Bipyridyl Complexes.** Figure 2 shows the cyclic voltammograms of \([\text{Ru(bpy)}_2(\text{CO})\text{Cl}]^+\) and \([\text{Ru(bpy)}_2(\text{CO})_2]^2\) by using a hanging mercury drop electrode (HMDE) with the surface area of 2.22 ± 0.07 mm² in DMF under \(\text{N}_2\) and \(\text{CO}_2\) atmospheres. The cyclic voltammogram of \([\text{Ru(bpy)}_2(\text{CO})\text{Cl}]^+\) in an \(\text{N}_2\)-saturated DMF solution shows two redox couples in the potential range −0.50 to −1.60 V vs. SCE. (a solid line in Figure 2a). The peak separations between the cathodic and anodic waves of the redox reactions at \(E_{1/2} = -1.21\) and −1.41 V vs. SCE are 60 and 90 mV, respectively, at a sweep rate of 0.10 V s⁻¹. The peak potential of the former couple was independent of the sweep rate in the range 0.50–0.05 V s⁻¹. On the other hand, the anodic wave of the latter couple almost disappeared at a sweep rate of 0.05 V s⁻¹, while the corresponding cathodic wave is still observed clearly at −1.48 V vs. SCE.
The cyclic voltammogram of \([\text{Ru(bpy)}_2\text{(CO)}]^{2+}\) in CO₂-saturated DMF, at a sweep rate of 0.20 V s⁻¹, reveals two new bands at 350 and 420 nm in its electronic absorption spectrum, which is consistent with that of a DMF solution containing \([\text{Ru(bpy)}_2\text{(CO)}]^{2+}\) and 2 mol equiv of n-Bu₄NOH. Instead, a cathodic wave at -1.40 V vs. SCE in CO₂-saturated DMF (dashed lines in parts a and b, respectively, of Figure 2) can be essentially the same as those of the corresponding complexes in N₂-saturated DMF, except that strong cathodic currents begin to flow around -1.40 V vs. SCE in CO₂-saturated DMF (compare solid lines and dashed lines in parts a and b of Figure 2). Removal of CO₂ from CO₂-saturated DMF solutions of \([\text{Ru(bpy)}_2\text{(CO)}_2\text{Cl}]^{2+}\) and \([\text{Ru(bpy)}_2\text{(CO)}_2\text{Cl}]^{2+}\) by bubbling N₂ through the solution for 1 h resulted in complete disappearance of the strong cathodic currents to give the cyclic voltammograms of those complexes in N₂-saturated DMF solutions. Thus, in the presence of \([\text{Ru(bpy)}_2\text{(CO)}]^{2+}\) or \([\text{Ru(bpy)}_2\text{(CO)}_2\text{Cl}]^{2+}\), CO₂ can be reduced to -1.40 V vs. SCE.

As reported in a previous paper, \([\text{Ru(bpy)}_2\text{(CO)}_2\text{Cl}]^{2+}\) smoothly reacts with 1 and 2 mol equiv of OH⁻ to afford \([\text{Ru(bpy)}_2\text{(CO)}_2\text{Cl(OH)}]^{2+}\) (eq 5) and its deprotonated species \([\text{Ru(bpy)}_2\text{(CO)}_2\text{(COO)}]^{2+}\) (eq 6), respectively. In accordance with this, the irreversible cathodic wave at -0.95 V of the \([\text{Ru(bpy)}_2\text{(CO)}_2\text{Cl}]^{2+}\) redox couple completely disappeared in the cyclic voltammogram of a DMF solution containing \([\text{Ru(bpy)}_2\text{(CO)}_2\text{Cl}]^{2+}\) and 2 mol equiv of a methanolic solution of n-Bu₄NOH. Instead, a cathodic wave appeared at -1.40 V. In addition, the controlled potential electrolysis of \([\text{Ru(bpy)}_2\text{(CO)}_2\text{Cl}]^{2+}\) in CO₂-saturated DMF at -1.10 V shows two new bands at 350 (shoulder) and 420 nm in its electronic absorption spectrum, as shown in Figure 3, which is consistent with that of a DMF solution containing \([\text{Ru(bpy)}_2\text{(CO)}_2\text{Cl}]^{2+}\) and 2 mol equiv of n-Bu₄NOH. These results suggest that the two-electron reduction product of \([\text{Ru(bpy)}_2\text{(CO)}_2\text{Cl}]^{2+}\) reacts with CO₂ to afford \([\text{Ru(bpy)}_2\text{(CO)}_2\text{(COO)}]^{2+}\), which is further reduced to -1.40 V.


tion containing LiCl (0.10 mol dm\(^{-3}\)) as a supporting electrolyte and \([R~(bpy)~(C0)_3]^{+}\) (5.0 \(\times\) 10\(^{-4}\) mol dm\(^{-3}\)) in a CO\(_2\)-saturated anhydrous DMF solution containing a C0\(_2\)-saturated H\(_2\)O/DMF (1:1, v/v) solution. However, the same electrolysis of a C0\(_2\)-saturated anhydrous DMF solution containing LiCl (0.10 mol dm\(^{-3}\)) as a supporting electrolyte at 303 K.

**Reduction of CO\(_2\)** The controlled potential electrolysis of a CO\(_2\)-saturated anhydrous DMF solution containing \(n\)-Bu\(_4\)NClO\(_4\) as a supporting electrolyte and [Ru(bpy)\(_2\) (CO)]\(^{2+}\) 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% CO on the basis of the amount of [Ru(bpy)\(_2\)(CO)]\(^{2+}\).

However, the same electrolysis of a CO\(_2\)-saturated H\(_2\)O/DMF (1:1, v/v) solution containing LiCl (0.10 mol dm\(^{-3}\)) as a supporting electrolyte and [Ru(bpy)\(_2\)(CO)]\(^{2+}\) (5.0 \(\times\) 10\(^{-4}\) mol dm\(^{-3}\)) catalytically produces HCOO\(^-\) and CO (eq 2 and 3). The reduction of CO\(_2\) by the electrochemically (-1.50 V vs. SCE) reduced species Re(bpy)(CO)Cl in CO\(_2\)-saturated CH\(_3\)CN, where the reduction of CO\(_2\) takes place according to eq 9. Thus, the present CO\(_2\) reduction does not result from an oxide-reduction reaction shown in eq 9.

\[2\text{CO}_2 + 2e^- \rightarrow \text{CO} + \text{CO}_3^{2-} \quad (9) \]

As shown in Figure 4, the amount of CO formed increases linearly with the number of coulombs consumed in the reduction of CO\(_2\) up to 60 coulombs, and thereafter the rate of CO evolution gradually decreases. On the other hand, the amount of HCOO\(^-\) formed slowly increases during the consumption of the initial 60 coulombs and thereafter rapidly increases. The turnover numbers for the formation of CO and HCOO\(^-\) based on [Ru(bpy)\(_2\)(CO)]\(^{2+}\) are 26.2 and 18.2, respectively, when the reduction consumed 100 coulombs, as summarized in entry 1 in Table I. An increase and a decrease of the rates for the formation of HCOO\(^-\) and HCOO\(^-\) with a lapse of time may be associated with the decomposition of the complex to yield a black precipitate with liberation of only about 10% CO on the basis of the amount of [Ru(bpy)\(_2\)(CO)]\(^{2+}\).

\[\text{HCOO}^- + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2 \quad (4) \]

The amount of CO dissolved in DMF solution has not been determined.

**Figure 4.** Plots of the amounts of products vs. the coulomb number consumed in the electrolysis (-1.50 V vs. SCE) of CO\(_2\)-saturated H\(_2\)O/DMF (1:1, v/v) solution containing [Ru(bpy)\(_2\)(CO)]\(^{2+}\) (5.0 \(\times\) 10\(^{-4}\) mol dm\(^{-3}\)) and LiCl (0.10 mol dm\(^{-3}\)) as a supporting electrolyte at 303 K.

**Figure 5.** Plots of the amounts of products vs. the coulomb number consumed in the electrolysis (-1.50 V vs. SCE) of CO\(_2\)-saturated H\(_2\)O (pH 6.0)/DMF (9:1, v/v) solutions of (a) [Ru(bpy)\(_2\)(CO)]\(^{2+}\)(PF\(_6\)) and (b) [Ru(bpy)\(_2\)(CO)Cl](PF\(_6\)) (5.0 \(\times\) 10\(^{-4}\) mol dm\(^{-3}\)) buffered with H\(_3\)PO\(_4\)-NaOH.

CO\(_2\), 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 reactions 3 and 4. In accordance with this, the electrolysis of a CO\(_2\)-saturated H\(_2\)O (pH 6.0 buffered with H\(_3\)PO\(_4\)-NaOH)/DMF mixture (9:1, v/v) containing [Ru(bpy)\(_2\)(CO)]\(^{2+}\) produces only CO and \(\text{H}_2\), both of which linearly increase in amount with time, as shown in Figure 5a. No HCOO\(^-\) has been detected in solution even after the reduction consumed 100 coulombs (entry 2 in Table I). This is the case when [Ru(bpy)\(_2\)(CO)]\(^{2+}\) was used as a catalyst, as shown in Figure 5b. Similar results were obtained also in the reduction of CO\(_2\) in CO\(_2\)-saturated water at pH 6.0 and in a CO\(_2\)-saturated H\(_2\)O (pH 6.0)/DMF (1:1, v/v) mixture (entries 3 and 4, respectively, in Table I).

It is worthwhile to note that the amount of H\(_2\) evolved in the reduction of CO\(_2\) conducted in water at pH 6.0 is much larger than that in H\(_2\)O (pH 6.0)/DMF (1:1, v/v) (compare entries 3 with 4 in Table I). This is suggestive of the competitive reductions of CO\(_2\) and protons taking place. In fact, the amounts of CO and \(\text{H}_2\) formed increase and decrease, respectively, with the decreasing H\(_2\)O (pH G.0)/DMF ratios (entries 2-4 in Table I). It is noted that no HCOO\(^-\) has been formed at all irrespective of the proportion of water in H\(_2\)O (pH 6.0)/DMF mixtures.

The electrolysis of a CO\(_2\)-saturated alkaline solution, H\(_2\)O (pH 9.5)/DMF (9:1, v/v), of [Ru(bpy)\(_2\)(CO)]\(^{2+}\) or [Ru(bpy)\(_2\)(CO)Cl]\(^{+}\) catalytically produces HCOO\(^-\) together with CO and \(\text{H}_2\) without an induction period, and the amounts of HCOO\(^-\) and CO increase linearly with the progress of the reaction, as shown in part a or b of Figure 6. It is well-known that CO\(_2\) readily reacts with OH\(^-\) in alkaline solutions to afford HCO\(_3\)\(^-\) and CO\(_3^{2-}\), which exist as equilibrium mixture with CO\(_2\) in solutions.


Electrochemical CO₂ Reduction

Controlled potential electrolysis of an aqueous solution of Na₂CO₃ or NaHCO₃ (0.10 mol dm⁻³) in place of CO₂ in the presence of [Ru(bpy)₂(CO)₂]⁺ at -1.50 V vs. SCE, however, has produced only a stoichiometric amount of HCOO⁻ without CO evolution even after 50 coulombs was consumed in the reduction. Moreover, the electrolysis of an H₂O (pH 9.5)/DMF (9:1, v/v) solution of HCOONa (0.10 mol dm⁻³) in the presence of [Ru(bpy)₂(CO)₂]⁺ at -1.50 V has produced only H₂, suggesting that the conversion of HCOO⁻ to CO does not take place under the present electrolysis condition (eq 10).

\[
\text{HCOO}^- \rightarrow \text{CO} + \text{OH}^- \quad (10)
\]

Active Species in the Reduction of CO₂. As described above, the reduction of CO₂ in H₂O (pH 9.5)/DMF (9:1, v/v) produces HCOO⁻ as well as CO as main products. The formation of HCOO⁻ upon decreasing the proton concentrations may be associated with the shift of an equilibrium among [Ru(bpy)₂(CO)₂]²⁺, [Ru(bpy)₂(CO)(C(O)(OH))⁺, and [Ru(bpy)₂(CO)(COO⁻)]⁺ in solutions (eq 5 and 6). The equilibrium constants \( K_1 = 1.32 \times 10^5 \) mol⁻¹ dm³ and \( K_2 = 2.27 \times 10^4 \) mol⁻¹ dm³ for eq 5 and 6, respectively, in water at 298 K have little changed from those in an H₂O (at various pH)/DMF (9:1, v/v) mixture, as confirmed from the comparison of the electronic absorptions of [Ru(bpy)₂(CO)₂]²⁺ in both solvents. The distribution curves of [Ru(bpy)₂(CO)₂]²⁺, [Ru(bpy)₂(CO)(C(O)(OH))⁺, and [Ru(bpy)₂(CO)(COO⁻)]⁺ calculated from the equilibrium constants \( K_1 \) and \( K_2 \) in H₂O are depicted in Figure 7, which indicates that only [Ru(bpy)₂(CO)(COO⁻)]⁺ exists as a stable species in acidic conditions. Therefore, [Ru(bpy)₂(CO)₂]²⁺ may be a precursor for the production of CO in the reduction of CO₂ conducted in H₂O (pH 6.0)/DMF (9:1, v/v).

In weak alkaline solutions, however, [Ru(bpy)₂(CO)₂]²⁺, [Ru(bpy)₂(CO)(C(O)(OH))⁺, and [Ru(bpy)₂(CO)(COO⁻)]⁺ coexist as an equilibrium mixture; for instance, the proportion of these three ruthenium species in H₂O at pH 9.5 are 12.5:51.0:36.5. The electrolysis of a weak alkaline solution such an H₂O (pH 9.5)/DMF (9:1, v/v) mixture saturated with CO₂ produces a mixture of HCOO⁻ and CO in nearly equivalent amounts. This is suggestive of [Ru(bpy)₂(CO)(C(O)(OH))⁺ or [Ru(bpy)₂(CO)(COO⁻)]⁺ as being a precursor for the formation of HCOO⁻. This is consistent with the result that the electrolysis of an aqueous solution of [Ru(bpy)₂(CO)₂]²⁺ at -1.50 V has produced a stoichiometric amount of HCOO⁻ at pH 11.0 (buffered with Na₂CO₃), where [Ru(bpy)₂(CO)(COO⁻)]⁺ is a small amount of [Ru(bpy)₂(CO)(COO⁻)]⁺. For further clarification of the precursor for the formation of HCOO⁻ in the reduction of CO₂, the reduction potentials of [Ru(bpy)₂(CO)(C(O)(OH))⁺ and [Ru(bpy)₂(CO)(COO⁻)]⁺ were examined. The cyclic voltammogram of [Ru(bpy)₂(CO)₂]²⁺ in H₂O at pH 10.5, where [Ru(bpy)₂(CO)₂]²⁺ is almost completely converted to [Ru(bpy)₂(CO)(C(O)(OH))⁺ and [Ru(bpy)₂(CO)(COO⁻)]⁺ (Figure 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 when the pH value was increased, suggesting that the reduction involves the participation of two electrons together with one proton. The proton may participate in the diffusion-controlled equilibrium reaction between [Ru(bpy)₂(CO)(C(O)(OH))⁺ and [Ru(bpy)₂(CO)(COO⁻)]⁺ (eq 6), either of which undergoes a two-electron reduction to produce HCOO⁻.

Mechanisms of the Reduction of CO₂. A most plausible mechanism of the reduction of CO₂ in this system is presented in Scheme I. [Ru(bpy)₂(CO)₂]²⁺ undergoes an irreversible two-electron reduction at -0.95 V vs. SCE to give [Ru(bpy)₂(CO)₂]²⁺ with 20 electrons, which may liberate CO, generating pentacoordinated [Ru(bpy)₂(CO)]⁰ with 18 electrons, though unstable. In the absence of CO₂ in solutions, [Ru(bpy)₂(CO)]⁰ thus formed may be oxidized by a proton to afford [Ru(bpy)₂(CO)(OH)]⁺, which reacts with another proton to evolve H₂. In the presence of a large excess of CO₂, however, to produce [Ru(bpy)₂(CO)(C(O)(OH))⁻ possibly via [Ru(bpy)₂(CO)(COO⁻)]⁻, this is consistent with the fact that CO₂ rapidly reacts with a variety of bases B, such as OH⁻, RO⁻, R⁻, and R₄N⁺ (R = alkyl group; n = 0–3), to yield the 1:1 adducts B–CO₂⁻.
Of various \( \pi^2 \)-CO\(_2\) metal complexes reported so far, \(^{34-41}\) \([\text{W(CO)}_3\text{CO}]^2\) formed in the reaction of \([\text{W(CO)}_3]^+\) with CO\(_2\) at 185 K undergoes an oxide-transfer reaction with another CO\(_2\) molecule to produce \([\text{W(CO)}_3]^+\) and CO\(_2\)^{2+} at room temperature.\(^{34}\) Although \([\text{Ru(bpy)}_2(\text{CO})(\text{COO}^-)]^+\) does not undergo such an oxide transfer reaction with another CO\(_2\) molecule, it may easily be converted to \([\text{Ru(bpy)}_2(\text{CO})]^{2+}\) via \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})\text{OH}]^+\)^{24} in acidic conditions according to the equilibrium reactions shown in eq 5 and 6 and in Scheme I. Thus, the reduction of CO\(_2\) conducted in acidic media produces only CO. On the other hand, in weak alkaline solutions such as pH 9.5, \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})\text{OH}]^+\) (or \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})\text{OH})^+\) exists as a predominant species (Figure 7), which may undergo a two-electron reduction involving participation of one proton to give HCOO\(^-\) with regeneration of the penta-coordinated ruthenium(0) complex \([\text{Ru(bpy)}_2(\text{CO})]^2+\). The evolution of CO as the same time may come from \([\text{Ru(bpy)}_2(\text{CO})]^{2+}\) existing as a minor component (Figure 7) in the solution.

As described in a previous section, there is a close similarity between \([\text{Ru(bpy)}_2(\text{CO})]^{2+}\) and \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})]^{2+}\) as catalysts for the reduction of CO\(_2\), suggesting that the two-electron reduction of \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})]^{2+}\) results in the dissociation of CO\(_2\) to afford the unstable penta-coordinated intermediate \([\text{Ru(bpy)}_2(\text{CO})]^{2+}\)^{4+}, which reacts with CO\(_2\) to generate \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})(\text{CO})]^{2+}\)^{4+}. Several attempts to identify the formation of \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})(\text{CO})]^{2+}\) in an electrochemical two-electron reduction of \([\text{Ru(bpy)}_2(\text{CO})]^{2+}\) at \(-1.40 \text{ to } -1.50 \text{ V vs. SCE in CO}_2\)-saturated anhydrous DMF, however, have given only an insoluble black precipitate. This may result from instability of \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})(\text{CO})]^{2+}\) in anhydrous DMF at that potential. It is well-known that \([\text{Ru(bpy)}_2XY]^{2+} (X, Y = \text{pyridine derivatives}, \text{halides, phosphines, and so on}; n = 0 \text{ or } 2) \) undergoes two successive one-electron reversible or quasi-reversible reductions\(^{42}\) and the added electrons are considered to be localized mainly in \(\pi\)-orbitals of the bipyridine ligands.\(^{43,44}\) A strong \(\pi\)-electron acceptor CO ligand may, however, resist such an electron localization in \([\text{Ru(bpy)}_2(\text{CO})]^{2+}\) and \([\text{Ru(bpy)}_2(\text{CO})Cl]^{+}\). Thus, two-electron reductions of \([\text{Ru(bpy)}_2(\text{CO})]^{2+}\) and \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})]^{2+}\) may be followed by chemical reactions possibly to generate \([\text{Ru(bpy)}_2(\text{CO})]^{+}\). The participation of \([\text{Ru}(\text{bpy})_2(\text{CO})]^{+}\) in the catalytic cycle of the present CO\(_2\) reduction reasonably explains the formation of CO and HCOO\(^-\) depending on the pH of the solutions.

Registry No. CO\(_2\), 124-38-9; CO, 630-08-0; HCOO\(^-\), 71-47-6; \([\text{Ru(bpy)}_2(\text{CO})]^{2+}\), 105453-70-1; \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})]^{2+}\), 86389-98-2; \([\text{Ru(bpy)}_2(\text{CO})Cl]^{+}\), 105399-80-2; \([\text{Ru(bpy)}_2(\text{CO})(\text{CO})\text{OH}]^{+}\), 105373-59-9.

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**MNDO Calculations for Compounds Containing Germanium**

Michael J. S. Dewar, Gilbert L. Grady, and Eamonn F. Healy

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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MNDO has been parametrized for germanium. Calculations are reported for a number of compounds of germanium. The results are comparable with those for the third-period elements.

**Introduction**

The MNDO method\(^2\)\(^3\) is now established\(^4\) as a practical procedure for studying behavior, giving results comparable\(^5\) with those from quite good ab initio models (e.g., 4-31G) while requiring only one-thousandth as much computer time. Parameters are currently available for hydrogen,\(^6\) for the second period elements beryllium,\(^7\) boron,\(^8\) carbon,\(^9\) nitrogen,\(^2\) oxygen,\(^2\) and fluorine,\(^2\) for the third-period elements aluminum,\(^2\) silicon,\(^2\) phosphorus,\(^2\) sulfur,\(^2\) and chlorine,\(^2\) and for bromine,\(^2\) iodine,\(^2\) and tin.\(^2\)

\(^1\) Deceased January 28, 1986.

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**References**