Electrochemical CO_2 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 $HCOO^-$

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The controlled potential electrolysis of CO_2-saturated H_2O (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 H_2. The same electrolysis of a CO_2-saturated alkaline solution, H_2O (pH 9.5)/DMF (9:1, v/v), gives not only CO and H_2 but also $HCOO^-$. The effect of pH on the formation of CO and $HCOO^-$ in the reduction of CO_2 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 CO_2 to afford $[Ru(bpy)_2(CO)(COO^-)]^+$, which reacts with protons to produce $[Ru(bpy)_2(CO)C(O)OH]^+$ in weak alkaline conditions. The resulting $[Ru(bpy)_2(CO)C(O)OH]^+$ is further converted to $[Ru(bpy)_2(CO)_2]^{2+}$ by dehydroxylation in acidic conditions. The $[Ru(bpy)_2(CO)C(O)OH]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$ 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 CO_2 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,[11-16] and thermal[17-21] reductions of CO_2 have been studied by using homogeneous catalysts. Of these, the electrochemical reduction of CO_2 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 CO_2 giving $CO_2^{\bullet -}$ requires more negative potentials than −2.10 V vs. SCE (eq 1).[10]

$$CO_2 + e^- \rightarrow CO_2^{\bullet -} \quad (E^0 = -2.10\ V) \qquad (1)$$

However, CO_2 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 H_2/H^+ couple at pH 7.0 (eq 4).[11] In order to depress

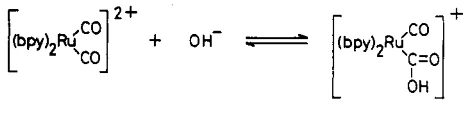
$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \quad (E^0 = -0.85\ V) \qquad (2)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (E^0 = -0.76\ V) \qquad (3)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (E^0 = -0.65\ V) \qquad (4)$$

the evolution of H_2 in the course of reduction of CO_2, therefore, it is desirable to use any catalysts which have a strong affinity for CO_2 even in the presence of protons. Of a number of transition-metal complexes as catalysts for the reduction of CO_2, rhenium 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 $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2′-bipyridine) undergoes a nucleophilic attack of OH^- in a weak alkaline aqueous solution to afford $[Ru(bpy)_2(CO)C(O)OH]^+$ (eq 5), which further reacts with OH^- at pH >9 to give a deprotonated species, $[Ru(bpy)_2(CO)(COO^-)]^+$ (eq 6).[22] The deprotonated species may be considered as an η^1-CO_2 adduct of Ru(0), $[Ru(bpy)_2(CO)(COO)]^0$, which may be



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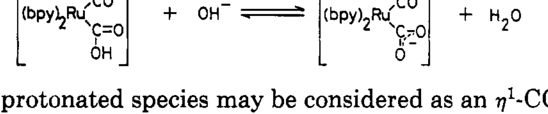

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unstable owing to the apparent 20-electron configuration around the central ruthenium atom. For the same reason, the two-electron reduction product of $[Ru(bpy)_2(CO)_2]^{2+}$ may be unstable to liberate one molecule of CO. Pentacoordinated Ru(0) thus formed may be oxidized by CO_2 and stabilized to generate $[Ru(bpy)_2(CO)(COO^-)]^+$, which may be converted to $[Ru(bpy)_2(CO)_2]^{2+}$ 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 CO_2 catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$.[3] This paper reports the catalytic cycle involving $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(bpy)_2(CO)]^0$, $[Ru(bpy)_2(CO)(COO^-)]^+$, and $[Ru(bpy)_2(CO)C(O)OH]^+$ as intermediates or active species to generate CO and $HCOO^-$ in the electrochemical reduction of CO_2.

Experimental Section

Materials. $Ru(bpy)_2Cl_2{\cdot}2H_2O$,[23] $[Ru(bpy)_2(CO)Cl](PF_6)$,[22] and $[Ru(bpy)_2(CO)_2](PF_6)_2$[22] were prepared according to the literatures. Commercially available guaranteed reagent grades of LiCl, NaOH, H_3PO_4, $NaHCO_3$, Na_2CO_3, and n-Bu_4NOH were used without further purification. n-Bu_4NClO_4 prepared by the reaction of n-Bu_4NBr 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 pressure.

Physical Measurements. Electrochemcial 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 ± 0.07 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), 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).[24]

Electrochemical Reduction of CO_2. The reduction of CO_2 in a CO_2-saturated H_2O/DMF mixture containing $[Ru(bpy)_2(CO)_2]^{2+}$ or $[Ru(bpy)_2(CO)Cl]^+$ was carried out by the controlled potential electrolysis at −1.50 V vs. SCE on an Hg electrode. The electrolysis cell[25] consisted of three compartments (Figure 1): one for an Hg working electrode (3.1 cm^2), the second, separated from the working electrode cell by a glass frit, for a platinum auxiliary electrode (ca. 3 cm^2), and the third for an SCE reference electrode. The volume of these compartments were 35, 25, and 8 cm^3, respectively, and the former two connected to volumetric flasks with stainless steel tubes (i.d. = 0.4 mm). CO_2-saturated H_2O/DMF solutions containing $[Ru(bpy)_2(CO)_2]^{2+}$ or $[Ru(bpy)_2(CO)Cl]^+$ (0.50 mmol dm^{-3}, 50 cm^3) were prepared by mixing a CO_2-saturated DMF solution containing either the Ru(II) complex (0.025 mmol, 5–45 cm^3) with CO_2-saturated water (pH 6.0 or 9.5, 5–45 cm^3) buffered with H_3PO_4–NaOH (the ionic strength is 0.05). After a stream of CO_2 was passed from the working electrode compartment to the volumetric flask for 30 min to displace the air in the electrolysis cell, the CO_2-saturated H_2O/DMF solution (40 cm^3) containing $[Ru(bpy)_2(CO)_2]^{2+}$ or $[Ru(bpy)_2(CO)Cl]^+$ 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 CO_2 between the gaseous and liquid phases in the cell was confirmed from a constant height of the meniscus of CO_2-saturated water in the volumetric flasks connected to the working and auxiliary electrode compartments. The reduction of 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.

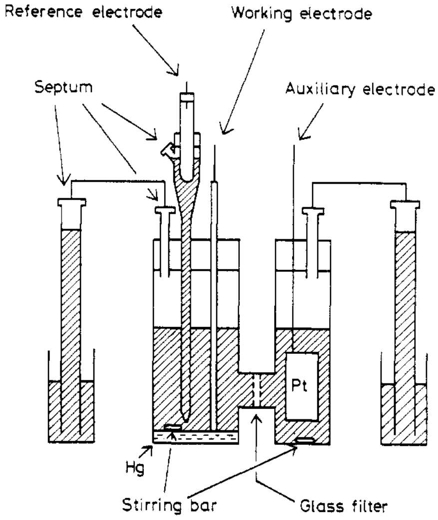

Figure 1. The electrolysis cell.

Product Analysis. At a fixed interval of coulombs consumed in the reduction, each 0.1-cm^3 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-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 N_2 as a carrier gas (for the determination of H_2 and 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-cm^3 portion from the working electrode compartment through a septum cap by syringe techniques 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 $Cd(NO_3)_2$ (6.0 mmol dm^{-3}) and caproic 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 $[Ru(bpy)_2(CO)Cl]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$ by using a hanging mercury drop electrode (HMDE) with the surface area of 2.22 ± 0.07 mm^2 in DMF under N_2 and CO_2 atmospheres. The cyclic voltammogram of $[Ru(bpy)_2(CO)Cl]^+$ in an 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 indepedent 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. Thus,

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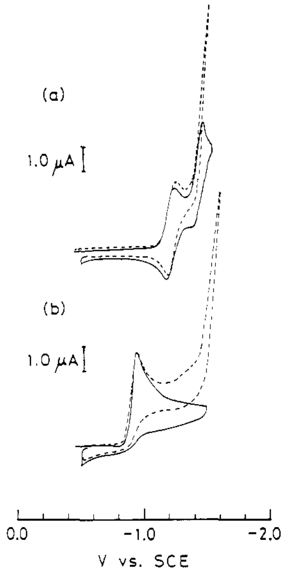

Figure 2. Cyclic voltammograms of (a) $[Ru(bpy)_2(CO)Cl]^+$ and (b) $[Ru(bpy)_2(CO)_2]^{2+}$ (5.0×10^{-4} mol dm^{-3}) in DMF containing n-Bu_4NClO_4 (0.10 mol dm^{-3}) as a supporting electrolyte under N_2 (—) and CO_2 (- - -) atmosphere, using an Hg electrode (sweep rate = 0.10 V s^{-1}).

$[Ru(bpy)_2(CO)Cl]^+$ undergoes two successive one-electron reductions; one is reversible reduction at −1.24 V and the other essentially an irreversible reduction around −1.48 V vs. SCE, confirming that the two-electron reduction of $[Ru(bpy)_2(CO)Cl]^+$ is followed by a slow chemical reaction.

The cyclic voltammogram of $[Ru(bpy)_2(CO)_2]^{2+}$ under N_2 atmosphere shows an irreversible cathodic wave at −0.95 V vs. SCE at a sweep rate of 0.10 V s^{-1} (a solid line in Figure 2b). If one assumes that the diffusion constant of $[Ru(bpy)_2(CO)_2]^{2+}$ is essentially identical with that of $[Ru(bpy)_2(CO)Cl]^+$ on the basis of their similar structures, the number of electrons consumed in the irreversible cathodic wave of $[Ru(bpy)_2(CO)_2]^{2+}$ at −0.95 V may be determined by using the diffusion constant of $[Ru(bpy)_2(CO)Cl]^+$ calculated from the reversible cathodic wave at −1.24 V vs. SCE as follows. 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 298 K as expressed by eq 7,[26] where n, A, D, v, and C^* are the number of electrons

$$i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}v^{1/2}C^* \qquad (7)$$

consumed in the redox reaction, the surface area (cm^2) of an electrode, the diffusion constant (cm^2 s^{-1}) of an electroactive species, a voltage sweep rate (V s^{-1}), and the bulk concentration (mol cm^{-3}) of an electroactive species, respectively. Thus, the diffusion constant of $[Ru(bpy)_2(CO)Cl]^+$ is determined as 3.0×10^{-6} cm^2 s^{-1} from a peak current of 2.3×10^{-6} A of the one-electron reversible cathodic wave at a sweep rate of 0.20 V s^{-1}.[27] On the other hand, the relationship between the peak current i_p(irr) and the diffusion constant D of an electroactive species, which undergoes a totally irreversible redox reaction, can be expressed by eq 8,[28] 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(irr) of the irreversible cathodic wave of $[Ru(bpy)_2(CO)_2]^{2+}$ at a sweep rate of 0.20 V s^{-1} were calculated as 60 mV and 4.5×10^{-6} A, respectively. Substitution of these values in eq 8 yields $n = 1.96$. Thus, $[Ru(bpy)_2(CO)_2]^{2+}$ undergoes an irreversible two-electron reduction around −0.95 V.

$$i_p(\mathrm{irr}) = (2.99 \times 10^5)n\left(\frac{47.7}{|E_p - E_{p/2}|}\right)^{1/2}AD^{1/2}v^{1/2}C^* \qquad (8)$$

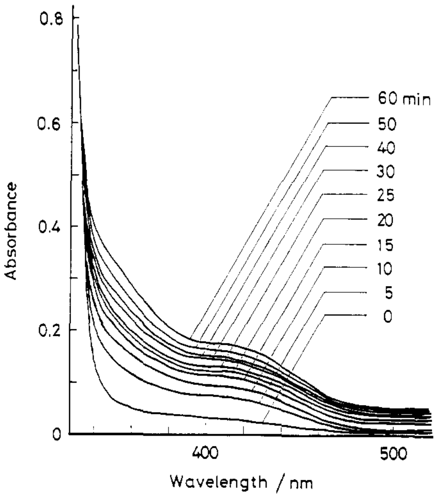

Figure 3. Electronic absorption spectra of a CO_2-saturated DMF solution of $[Ru(bpy)_2(CO)_2]^{2+}$ (5.0×10^{-4} mol dm^{-3}) under the controlled potential electrolysis at −1.10 V vs. SCE.

The cyclic voltammograms of $[Ru(bpy)_2(CO)Cl]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$ in CO_2-saturated DMF (dashed lines in parts a and b, respectively, of Figure 2) are essentially the same as those of the corresponding complexes in N_2-saturated DMF, except that strong cathodic currents begin to flow around −1.40 V vs. SCE in CO_2-saturated DMF (compare solid lines and dashed lines in parts a and b of Figure 2). Removal of CO_2 from CO_2-saturated DMF solutions of $[Ru(bpy)_2(CO)Cl]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$ by bubbling 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 N_2-saturated DMF solutions. Thus, in the presence of $[Ru(bpy)_2(CO)Cl]^+$ or $[Ru(bpy)_2(CO)_2]^{2+}$, CO_2 can be reduced to −1.40 V vs. SCE.

As reported in a previous paper,[22] $[Ru(bpy)_2(CO)_2]^{2+}$ smoothly reacts with 1 and 2 molar equiv of OH^- to afford $[Ru(bpy)_2(CO)C(O)OH]^+$ (eq 5) and its deprotonated species $[Ru(bpy)_2(CO)(COO^-)]^+$ (eq 6), respectively. In accordance with this, the irreversible cathode wave at −0.95 V of the $[Ru(bpy)_2(CO)_2]^{2+/0}$ redox couple completely disappeared in the cyclic voltammogram of a DMF solution containing $[Ru(bpy)_2(CO)_2]^{2+}$ and 2 molar equiv of a methanolic solution of n-Bu_4NOH. Instead, a cathodic wave appeared at −1.40 V. In addition, the controlled potential electrolysis of $[Ru(bpy)_2(CO)_2]^{2+}$ in CO_2-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 $[Ru(bpy)_2(CO)_2]^{2+}$ and 2 molar equiv of n-Bu_4NOH.[29] These results suggest that the two-electron reduction product of $[Ru(bpy)_2(CO)_2]^{2+}$ reacts with CO_2 to afford $[Ru(bpy)_2(CO)(COO^-)]^+$, which is further reduced to −1.40 V.

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[27] The diffusion constant of $[Ru(bpy)_3]^{2+}$ in DMF was determined as 3.2×10^{-6}/cm^2 s^{-1} by the same procedure, suggesting that the charge of the complexes does not influence significantly the diffusion constant.

[28] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 222.

[29] The absorptivity of $[Ru(bpy)_2(CO)(COO^-)]^+$ formed in the electrolysis of $[Ru(bpy)_2(CO)_2]^{2+}$ at −1.10 V for 60 min in CO_2-saturated DMF was about 60% based on that formed in the reaction of $[Ru(bpy)_2(CO)_2]^{2+}$ with 2 molar equiv of n-Bu_4NOH in DMF since a prolonged electrolysis of $[Ru(bpy)_2(CO)_2]^{2+}$ under anhydrous conditions results in a partial decomposition even at −1.10 V.

Table I. Electrochemical CO_2 Reduction Catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ (1) and $[Ru(bpy)_2(CO)Cl]^+$ (2) in H_2O/DMF Systems

entry	cat.[a]	H_2O/DMF (v/v)	pH[b]	coulombs consumed	product, μmol CO	H_2	$HCOO^-$
1	1	1/1	not fixed[c]	100	262	2	182
2	1	9/1	6.0	100	142	182	
3	1	1/0	6.0	100	88	282	
4	1	1/1	6.0	100	217	18	
5	1	9/1	9.5	100	136	192	199
6	2	1/1	not fixed[c]	90	255	21	78
7	2	9/1	6.0	100	107	217	
8	2	9/1	9.5	75	110	170	101

[a] PF_6 salt = 5.0×10^{-4} mol dm^{-3}, 20 cm^3. [b] Buffered with H_3PO_4–NaOH. [c] LiCl used as an electrolyte.

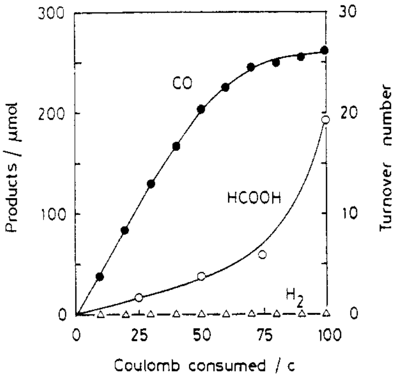

Figure 4. Plots of the amounts of products vs. the coulomb number consumed in the electrolysis (−1.50 V vs. SCE) of CO_2-saturated H_2O/DMF (1:1, v/v) solution containing $[Ru(bpy)_2(CO)_2](PF_6)_2$ (5.0×10^{-4} mol dm^{-3}) and LiCl (0.10 mol dm^{-3}) as a supporting electrolyte at 303 K.

Reduction of CO_2. The controlled potential electrolysis of a CO_2-saturated anhydrous DMF solution containing n-Bu_4NClO_4 as a supporting electrolyte and $[Ru(bpy)_2(CO)_2]^{2+}$ 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 $[Ru(bpy)_2(CO)_2]^{2+}$.[30] However, the same electrolysis of a CO_2-saturated H_2O/DMF (1:1, v/v) solution containing LiCl (0.10 mol dm^{-3}) as a supporting electrolyte and $[Ru(bpy)_2(CO)_2]^{2+}$ (5.0×10^{-4} mol dm^{-3}) catalytically produces $HCOO^-$ and CO (eq 2 and 3) together with a small amount of H_2 (eq 4), as shown in Figure 4. This result is in contrast to the catalytic reduction of CO_2 by the electrochemically (−1.50 V vs. SCE) reduced species $Re(bpy)(CO)_3Cl$ in CO_2-saturated CH_3CN, where the reduction of CO_2 takes place according to eq 9.[2] Thus, the present CO_2 reduction does not result from an oxide-transfer reaction shown in eq 9.

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-} \qquad (9)$$

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 inital 60 coulombs and thereafter rapidly increases. The turnover numbers for the formation of CO and $HCOO^-$ based on $[Ru(bpy)_2(CO)_2]^{2+}$ are 26.2 and 18.2, respectively, when the reduction consumed 100 coulombs, as summarized in entry 1 in Table I. A similar result was obtained also in the reduction of CO_2 by $[Ru(bpy)_2(CO)Cl]^+$ under the same electrolysis condition (entry 6 in Table I). An increase and a decrease of the rates for the formation of $HCOO^-$ 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 reactions 3 and 4. In accordance with this, the electrolysis of a CO_2-saturated H_2O (pH 6.0 buffered with H_3PO_4–NaOH)/DMF mixture (9:1, v/v) containing $[Ru(bpy)_2(CO)_2]^{2+}$ produces only CO and 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 $[Ru(bpy)_2(CO)Cl]^+$ 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_2O (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_2O (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 H_2 formed increase and decrease, respectively, with the decreasing H_2O (pH 6.0)/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_2O (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 I).

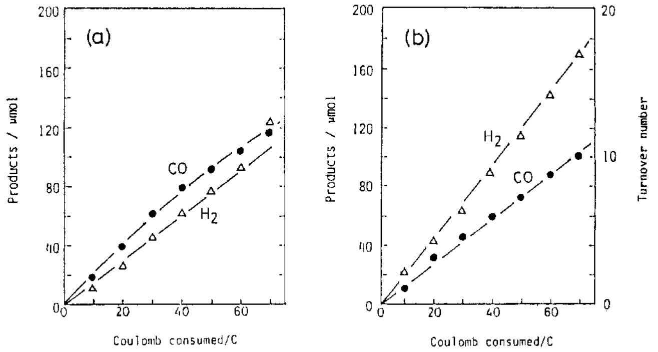

Figure 5. Plots of the amounts of products vs. the coulomb number consumed in the electrolysis (−1.50 V vs. SCE) of CO_2-saturated H_2O (pH 6.0)/DMF (9:1, v/v) solutions of (a) $[Ru(bpy)_2(CO)_2](PF_6)_2$ and (b) $[Ru(bpy)_2(CO)Cl](PF_6)$ (5.0×10^{-4} mol dm^{-3}), buffered with H_3PO_4–NaOH.

The electrolysis of a CO_2-saturated alkaline solution, H_2O (pH 9.5)/DMF (9:1, v/v), of $[Ru(bpy)_2(CO)_2]^{2+}$ or $[Ru(bpy)_2(CO)Cl]^+$ catalytically produces $HCOO^-$ together with CO and 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 an an equilibrium mixture with CO_2 in solutions.[31] The

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

[31] Kern, D. M. *J. Chem. Educ.* **1960**, *37*, 14.

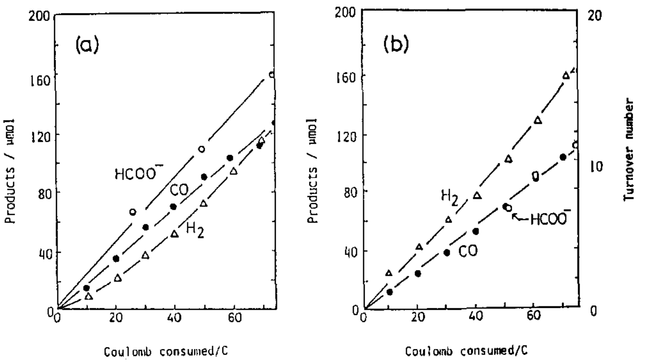


Figure 6. Plots of the amounts of products vs. the coulomb number consumed in the electrolysis (−1.50 V vs. SCE) of CO_2-saturated H_2O (pH 9.5)/DMF (9:1, v/v) solutions of (a) $[Ru(bpy)_2(CO)_2](PF_6)_2$ and (b) $[Ru(bpy)_2(CO)Cl](PF_6)$ (5.0×10^{-4} mol dm^{-3}), buffered with H_3PO_4–NaOH.

controlled potential electrolysis of an aqueous solution of Na_2CO_3 or $NaHCO_3$ (0.10 mol dm^{-3}) in place of CO_2 in the presence of $[Ru(bpy)_2(CO)_2]^{2+}$ 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 H_2O (pH 9.5)/DMF (9:1, v/v) solution of HCOONa (0.10 mol dm^{-3}) in the presence of $[Ru(bpy)_2(CO)_2]^{2+}$ at −1.50 V has produced only H_2, suggesting that the conversion of $HCOO^-$ to CO does not take place under the present electrolysis condition (eq 10). Thus, the catalytic formation of CO and $HCOO^-$ in the electrolysis of a CO_2-saturated H_2O (pH 9.5)/DMF (9:1, v/v) solution of either $[Ru(bpy)_2(CO)_2]^{2+}$ or $[Ru(bpy)_2(CO)Cl]^+$ (entries 5 and 8 in Table I) may come from two different precursors.

$$HCOO^- \rightarrow CO + OH^- \qquad (10)$$

Active Species in the Reduction of CO_2. As described above, the reduction of CO_2 in H_2O (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} dm^3 and $K_2 = 2.27 \times 10^4$ mol^{-1} dm^3 for eq 5 and 6; respectively, in water at 298 K[22] have little changed from those in an H_2O (at various pH)/DMF (9:1, v/v) mixture, as confirmed from the comparison of the electronic absorption spectra 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 H_2O are depicted in Figure 7, which indicates that only $[Ru(bpy)_2(CO)_2]^{2+}$ 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 CO_2 conducted in H_2O (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 H_2O at pH 9.5 are 12.5:51.0:36.5. The electrolysis of a weak alkaline solution such an H_2O (pH 9.5)/DMF (9:1, v/v) mixture saturated with CO_2 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 Na_2CO_3), where $[Ru(bpy)_2(CO)(COO^-)]^+$ and a small amount of $[Ru(bpy)_2(CO)C(O)OH]^+$ exist. For further clarification of the precursor for the formation of $HCOO^-$ in the reduction of CO_2, 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 H_2O 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),[22] either of which undergoes a two-electron reduction to produce $HCOO^-$.

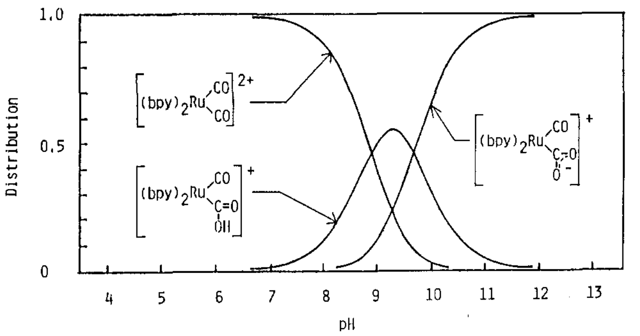
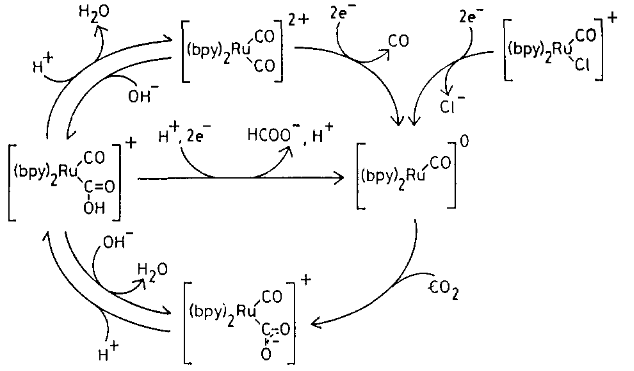


Figure 7. Distribution of the ruthenium species in H_2O at various pHs at 298 K.

Scheme I



Mechanisms of the Reduction of CO_2. A most plausible mechanism of the reduction of CO_2 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 $[Ru(bpy)_2(CO)_2]^0$ with 20 electrons, which may liberate CO, generating pentacoordinated $[Ru(bpy)_2(CO)]^0$ with 18 electrons, though unstable. In the absence of CO_2 in solutions, $[Ru(bpy)_2(CO)]^0$ thus formed may be oxidized by a proton to afford $[Ru(bpy)_2(CO)H]^+$,[32] which reacts with another proton to evolve H_2.[33] In the presence of a large excess of CO_2, however, to produce $[Ru(bpy)_2(CO)(COO^-)]^+$ possibly via $[Ru(bpy)_2(CO)(COO)]^0$. This is consistent with the fact that CO_2 rapidly reacts with a variety of bases B, such as OH^-, RO^-, R^-, and R_nNH_{3-n} (R = alkyl group; n = 0–3), to yield the 1:1 adducts B–COO^-.

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[32] The thermal decarboxylation of $[Ru(bpy)_2(CO)(COOH)]^+$ affording $[Ru(bpy)_2(CO)H]^+$ does not take place up to 373 K.[22]

[33] (a) Kelly, J. M.; Vos, J. G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 628. (b) Kelly, J. M.; Vos, J. G. *J. Chem. Soc., Dalton. Trans.* **1986**, 1045.

Of various η^1-CO_2 metal complexes reported so far,[34-41] $[W(CO)_5CO_2]^{2-}$ formed in the reaction of $[W(CO)_5]^{2-}$ with CO_2 at 195 K undergoes an oxide-transfer reaction with another CO_2 molecule to produce $[W(CO)_6]$ and $CO_3{}^{2-}$ at room temperature.[34] Although $[Ru(bpy)_2(CO)(COO^-)]^+$ does not undergo such an oxide transfer reaction with another CO_2 molecule, it may easily be converted to $[Ru(bpy)_2(CO)_2]^{2+}$ via $[Ru(bpy)_2(CO)C(O)OH]^+$ 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, $[Ru(bpy)_2(CO)C(O)OH]^+$ (or $[Ru(bpy)_2(CO)(COO^-)]^+$) 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 pentacoordinated ruthenium(0) complex $[Ru(bpy)_2(CO)]^0$. The evolution of CO as the same time may come from $[Ru(bpy)_2(CO)_2]^{2+}$ existing as a minor component (Figure 7) in the solution.

As described in a previous section, there is a close similarity between $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)Cl]^+$ as catalysts for the reduction of CO_2, suggesting that the two-electron reduction of $[Ru(bpy)_2(CO)Cl]^+$ results in the dissociation of Cl^- to afford the unstable pentacoordinated intermediate $[Ru(bpy)_2(CO)]^0$, which reacts with CO_2 to generate $[Ru(bpy)_2(CO)(COO^-)]^+$. Several attempts to identify the formation of $[Ru(bpy)_2(CO)(COO^-)]^+$ in an electrochemical two-electron reduction of $[Ru(bpy)_2(CO)Cl]^+$ at −1.40 to −1.50 V vs. SCE in CO_2-saturated anhydrous DMF, however, have given only an insoluble black precipitate. This may result from instability of $[Ru(bpy)_2(CO)(COO^-)]^+$ in anhydrous DMF at that potential. It is well-known that $[Ru(bpy)_2XY]^{n+}$ (X, Y = pyridine derivatives, halides, phosphines, and so on; n = 0–2) undergoes two successive one-electron reversible or quasireversible reductions[42] and the added electrons are considered to be localized mainly in π^*-orbitals of the bipyridine ligands.[43,44] A strong π-electron acceptor CO ligand may, however, resist such an electron localization in $[Ru(bpy)_2(CO)_2]^0$ and $[Ru(bpy)_2(CO)Cl]^-$. Thus, two-electron reductions of $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)Cl]^+$ may be followed by chemical reactions possibly to generate $[Ru(bpy)_2(CO)]^0$. The participation of $[Ru(bpy)_2(CO)]^0$ in the catalytic cycle of the present CO_2 reduction reasonably explains the formation of CO and $HCOO^-$ depending on pH of the solutions.

Registry No. CO_2, 124-38-9; CO, 630-08-0; $HCO_2{}^-$, 71-47-6; $[Ru(bpy)_2(CO)_2]^{2+}$, 105453-70-1; $[Ru(bpy)_2(CO)Cl]^+$, 86389-98-2; $[Ru(bpy)_2(CO)]^0$, 105399-80-2; $[Ru(bpy)_2(CO)(COO^-)]$, 86536-98-3; $[Ru(bpy)_2(CO)C(O)OH]^+$, 105373-59-9.

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MNDO Calculations for Compounds Containing Germanium[†1]

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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,[3] for the second period elements beryllium,[6] boron,[7] carbon,[3] nitrogen,[3] oxygen,[3] and fluorine,[8] for the third-period elements aluminum,[9] silicon,[10] phosphorus,[11] sulfur,[12] and chlorine,[13] and for bromine,[14] iodine,[15] and tin.[16] Since d AOs are not currently included in MNDO, calculations are confined to compounds involving only normal group

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[‡] Deceased January 28, 1986.

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