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NOTE

Selective formation of ketones by electrochemical reduction of CO_2 catalyzed by ruthenium complexes†

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Electrochemical reduction of CO_2 aimed at carbon–carbon bond formation was examined. Polypyridyl–ruthenium–carbonyl complexes catalyze electrochemical reduction of CO_2 to produce CO and CO_3^{2-} in organic solvents. Among those metal complexes, a ruthenium carbonyl complex with monodentate naphthyridine showed a unique redox behavior. One-electron reduction of the complex resulted in intramolecular nucleophilic attack of the non-bonded nitrogen of naphthyridine to the carbonyl carbon to form a five-membered ring. Such metallacyclization greatly served for activation of the Ru—CO bond derived from CO_2 without accompanying reductive cleavage of the bond (CO evolution). Electrochemical reduction of CO_2 catalyzed by $[Ru(bpy)(napy)_2(CO)_2]^{2+}$ in the presence of $(CH_3)_4NBF_4$ produced only $CH_3C(O)CH_3$ and CO_3^{2-}, where $(CH_3)_4N^+$ worked as not only the electrolyte but also the methylation reagent. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: carbon dioxide reduction; selective acetone formation; acyl intermediate; metallacyclization.

1 INTRODUCTION

A number of metal complexes have proven to be active in photo- and electro-chemical reductions of CO_2 producing CO and/or HCOOH.[1] Metal complexes with η^1–CO_2 are considered to play the key role in the reduction of CO_2, since metal—η^1–CO_2 is easily converted to metal—CO through an acid–base reaction in protic media (Eqn [1]) or via oxide transfer to free CO_2 in aprotic media (Eqn [2]). CO evolution in the reduction of CO_2 is ascribed to reductive cleavage of the resulting metal—CO bonds (Eqn [3]).[1]

$$[M\text{—}CO_2]^{n+} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [M\text{—}C(O)OH]^{(n+1)+} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [M\text{—}CO]^{(n+2)+} \quad [1]$$

$$[M(CO_2)]^{n+} + CO_2 \longrightarrow [M\text{—}CO]^{(n+2)+} + CO_3^{2-} \quad [2]$$

$$[M\text{—}CO]^{(n+2)+} + 2e^- \longrightarrow [M]^{n+} + CO \quad [3]$$

On the other hand, metal—CO complexes have been widely used as homogeneous catalysts for introduction of CO to organic groups under CO atmosphere. Thus, CO evolution in the reduction of CO_2 (Eqn [3]) is not suitable for carbon–carbon bond formation. Depression of CO evolution was achieved in electrochemical reduction of CO_2 catalyzed by $[Ru(bpy)(trpy)(CO)]^{2+}$ conducted at −20 °C in EtOH–H_2O, where H_2CO, CH_3OH, HOOCCHO and $HOOCCH_2OH$ were produced through $[Ru(bpy)(trpy)(CHO)]^+$.[2] The formyl complex, however, reacted with CO_2 even at −20 °C and $HCOO^-$ was generated as a main product with regeneration of $[Ru(bpy)(trpy)(CO)]^{2+}$ (Eqn [4]).[3]

$$[Ru(bpy)(trpy)(CO)]^{2+} \underset{HCOO^- \quad CO^2}{\overset{2e^-,\ H^+}{\rightleftharpoons}} [Ru(bpy)(trpy)(CHO)]^+ \quad [4]$$

Thus, multi-electron reduction of CO_2 through a formyl intermediate appears to have serious problems due to thermal lability and strong hydride donor ability of the complex. An alternative pathway from metal—CO to metal—C(O)R, therefore, may lead to a new methodology for the utilization of CO_2 as a C1 resource. This paper

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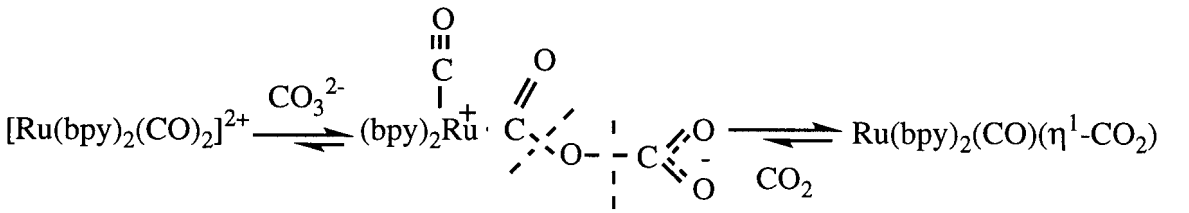


Scheme 1.

reports the first selective production of acetone in the reduction of CO_2 catalyzed by [Ru(bpy)(napy)$_2$(CO)$_2$](PF$_6$)$_2$ (napy = 1,8-naphthyridine-κN) in the presence of $(CH_3)_4NBF_4$.

2 REDUCTIVE DISPROPORTIONATION OF CO_2 ON RUTHENIUM

Three complexes, [Ru(bpy)$_2$(CO)(η^1-CO_2)], [Ru(bpy)$_2$(CO)(C(O)OH)]$^+$ and [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ exist as equilibrium mixtures in H_2O.[4] Reversible CO_2–CO conversion also took place through oxide transfer from [Ru(bpy)$_2$(CO)(η^1-CO_2)] to CO_2 and from CO_3^{2-} to [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ in CH_3CN (Scheme 1).[5] The equilibrium between [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ and [Ru(bpy)$_2$(CO)(η^1-CO_2)], however, lay so far towards the latter in DMSO under 1 atm CO_2. As a result, [Ru(bpy)$_2$(CO)(η^1-CO_2)] practically did not work as a catalyst to reduce CO_2 in the absence of a proton source (Eqns [2] and [3]). On the other hand, both [Ru(bpy)(trpy)(CO_2)] and [Ru(bpy)$_2$(qui)(CO_2)] (qui = quinoline) were rapidly converted to [Ru(bpy)(trpy)(CO)]$^{2+}$ and [Ru(bpy)$_2$(qui)(CO)]$^{2+}$ respectively under CO_2 atmosphere. For example, an addition of dry ice to a dark red CH_3CN solution of [Ru(bpy)$_2$(qui)(CH_3CN)]^0, prepared by the controlled potential electrolysis of [Ru(bpy)$_2$(qui)(CH_3CN)](PF$_6$)$_2$ at -1.60 *V* in the presence of $(CH_3)_4NBF_4$ under N_2, gave [Ru(bpy)$_2$(qui)(CO)]$^{2+}$ and $(Me_4N)_2CO_3$ (Eqns [5] and [6]) via [Ru(bpy)$_2$(qui)(CO_2)].

In accordance with the reactions of Eqns [5] and [6], the electrolysis of

$$[Ru(bpy)_2(qui)(CH_3CN)] + CO_2 \longrightarrow [Ru(bpy)_2(qui)(CO_2)] \quad [5]$$

$$[Ru(bpy)_2(qui)(CO_2)] + CO_2 \longrightarrow [Ru(bpy)_2(qui)(CO)]^{2+} + CO_3^{2-} \quad [6]$$

[Ru(bpy)$_2$(qui)(CO)]$^{2+}$ at -1.50 V in CO_2-saturated DMSO–CH_3CN in the presence of $LiBF_4$ evolved CO with a current efficiency of 78% with white precipitate of Li_2CO_3 (Eqns. [3] and [7]).

$$2CO_2 + 2e^- \longrightarrow CO + CO_3^{2-} \quad [7]$$

One- and two-electron reduction of [Ru(bpy)$_2$(qui)(CO)]$^{2+}$ under electrolysis at -1.21 and -1.50 V in CD_3CN resulted in the shift of the ν(CO) band from 2015 cm^{-1} to 1980 cm^{-1} and 1939 cm^{-1} respectively. Oxidation of the solution at 0 V essentially recovered the IR spectrum of [Ru(bpy)$_2$(qui)(CO)]$^{2+}$, although the intensity of ν(CO) decreased to some extent because of partial elimination of CO from [Ru(bpy)$_2$(qui)(CO)]^0 during the two-electron reduction–oxidation cycle (Eqn [3]). Moreover, [Ru(bpy)$_2$(qui)(CO)]^0 reacted with 2 equiv. of CH_3I to give $CH_3C(O)CH_3$ and [Ru(bpy)$_2$(qui)(CH_3CN)]$^{2+}$ (Eqn [8]).[6]

$$[Ru(bpy)_2(qui)(CO)] + 2CH_3I \longrightarrow CH_3C(O)CH_3 + [Ru(bpy)_2(qui)(CH_3CN)]^{2+} \quad [8]$$

This observation indicates that an Ru—CO complex derived from CO_2 can be utilized as an acyl intermediate in organic synthesis if two problems are overcome; one is the selective activation of CO_2 in the presence of alkylation reagents, and the other is depression of the reductive cleavage of the Ru—CO bond under reductive conditions.

3 COMPETITIVE REDUCTION OF CO_2 AND CH_3I

Figure 1 shows the amount of CH_3CH_3 produced in the controlled potential electrolysis of [Ru(bpy)(trpy)(CO)]$^{2+}$ or [Ru(bpy)$_2$(L)(CO)]$^{2+}$ (L = quinoline, 2-methylquinoline, *iso*-quinoline) in CO_2-saturated DMSO/CH_3CN (1:1 v/v) containing $(CH_3)_4NBF_4$ and 50 molar excess of CH_3I. When [Ru(bpy)(trpy)(CO)]$^{2+}$ was used as the catalyst, CH_3CH_3 is the main product (▼ in Fig. 1) and small

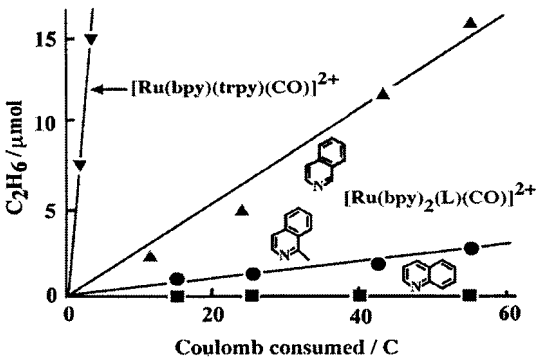


Figure 1 C_2H_6 evolved in the competitive reduction of CH_3I and CO_2 catalyzed by ruthenium complexes under the electrolysis conditions.

amounts of CO, CO_3^{2-} and $CH_3C(O)CH_3$ were produced. Assuming that $[Ru(bpy)(trpy)(CH_3)]^+$ is the precursor to C_2H_6 (Eqn [9]), $[Ru(bpy)(trpy)]^0$ formed by the reductive cleavage of the Ru—CO bond of $[Ru(bpy)(trpy)(CO)]^0$ undergoes the attack of CH_3I predominantly rather than CO_2.

$$2CH_3I + 2e^- \longrightarrow CH_3CH_3 + 2I^- \qquad [9]$$

On the other hand, the amounts of CH_3CH_3 evolved decreased substantially in the competitive reductions of CO_2 and CH_3I when $[Ru(bpy)_2(L)(CO)]^{2+}$ was used as the catalyst (Fig. 1). In particular, C_2H_6 evolution almost stopped and acetone was produced with a current efficiency around 20% in the reduction catalyzed by $[Ru(bpy)_2(qui)(CO)]^{2+}$. The decrease in the order of *iso*-quinoline > 2-methylquinoine > quinoline is explained by the steric hindrance of these ligands for the electrophilic attack of CH_3I to ruthenium (Fig. 2). Thus, the $Ru(bpy)_2(qui)$ framework is suitable for selective activation of CO_2 in the presence of a large excess of CH_3I.

Reductive activation of an Ru—CO bond without CO evolution by using an analog of the $Ru(bpy)_2(qui)$ framework, therefore, may provide a catalytic system that is capable of reducing CO_2 with formation of new carbon–carbon bonds.

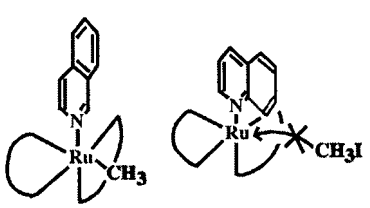
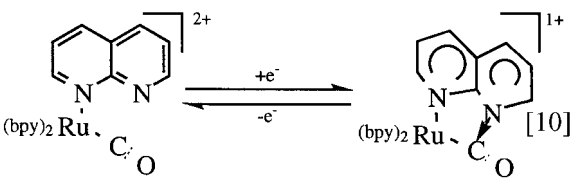


Figure 2 Steric hindrance of *iso*-quinoline and quinoline for attack of CH_3I to ruthenium.

4 INHIBITION OF REDUCTIVE CLEAVAGE OF THE Ru—CO BOND DERIVED FROM CO_2

The molecular structure of $[Ru(bpy)_2(napy)(CO)]^{2+}$ (napy = 1,8-naphthyridine-κN) is close to $[Ru(bpy)_2(qui)(CO)]^{2+}$, but the redox behavior of the two complexes is completely different. One-electron reduction of $[Ru(bpy)_2(napy)(CO)](PF_6)_2$ took place in a napy localized orbital. As a result, the carbonyl carbon underwent intramolecular nucleophilic attack by the non-bonded nitrogen of monodentate napy to form a five-membered ring, which caused pronounced bathochromic shift of the ν(CO) band ($\Delta = 418\ cm^{-1}$) (Eqn [10]).[7] The metallacyclization of Eqn [10] was



applied for the reductive activation of the Ru—CO bond without the accompanying reductive cleavage of the bond (CO evolution).

The cyclic voltammogram (CV) of $[Ru(bpy)_2(napy)(CO)](PF_6)_2$ in DMSO showed an irreversible cathodic wave at −1.40 V (vs Ag/Ag^+) and subsequent three (quasi-)reversible redox couples at $E_{1/2} = -1.33$, −1.40 and −1.57 V under N_2. The analog bis(napy) complex, $[Ru(bpy)(napy)_2(CO)_2](PF_6)_2$, displayed an irreversible cathodic wave at −1.15 V and quasi-reversible redox couples at $E_{1/2} = -1.80$ V. The irreversible cathodic waves at $E_{pc} = -1.42$ V and −1.15 V in the CV of $[Ru(bpy)_2(napy)(CO)]^{2+}$ and $[Ru(bpy)(napy)_2(CO)_2]^{2+}$ respectively are associated with the Ru—C(O)—N—*C*—*N* ring formation (Eqn. [10]). Introduction of CO_2 to the DMSO solution of $[Ru(bpy)(napy)_2(CO)_2]^{2+}$ caused strong catalytic currents due to the reduction of CO_2 at potentials more negative than −1.6 V, while the threshold potential of the CO_2 reduction by $[Ru(bpy)_2(napy)(CO)]^{2+}$ was close to −2.0 V. The controlled potential electrolysis of $[Ru(bpy)(napy)_2(CO)_2]^{2+}$

at −1.65 V (vs Ag/Ag^{2+}) with a glassy carbon electrode in CO_2-saturated DMSO containing $(CH_3)_4NBF_4$ produced $CH_3C(O)CH_3$ selectively with a trace amount of CO. Besides these products, $(CH_3)_3N$ and $\{(CH_3)_4N\}_2CO_3$ were formed and no other product was detected in the solution. Thus, $(CH_3)_4N^+$ worked as not only the electrolyte but also the methylation reagent for the catalytic generation of acetone in the electrochemical reduction of CO_2 catalyzed by $[Ru(bpy)(napy)_2(CO)_2]^{2+}$ (Eqn. [11]).

$$2CO_2 + 2(CH_3)_4N^+ + 4e^- \longrightarrow CH_3C(O)CH_3 + CO_3^{2-} + 2(CH_3)_3N \quad [11]$$

The rate of the acetone formation was greatly improved when the similar CO_2 reduction was conducted in the presence of CH_3I as a methylation agent. The selective formation of acetone in the electrochemical reduction of CO_2 (Eqn [11]) is ascribed to the suppression of reductive cleavage of the Ru—CO bond (Eq. [3]) by the metallacyclization of Eqn [10]. Indeed, the reduction of CO_2 catalyzed by $[Ru(bpy)(napy)_2(CO_2]^{2+}$ produced acetone without CO evolution.[8]

5 EXPERIMENTAL SECTION

Physical measurements

Infrared spectra were obtained on a Shimadzu FTIR-8300 spectrophotometer. ^1H NMR spectra were measured on a JEOL EX270 spectometer (270 MHz) with a temperature controller. Cyclic voltammetric experiments were performed with ALS/chi Model 660. The cell consisted of a glassy carbon working electrode (0.07 cm^2), a platinum wire auxiliary electrode and an $Ag/AgNO_3$ reference electrode.

IR spectra under electrolysis conditions were measured by the use of a thin-layer cell with a gold-mesh working electrode.[9]

Electrochemical reduction of CO_2

Electrochemical reduction of CO_2 was performed in the absence and the presence of alkylation agents CH_3I in CO_2-saturated CH_3CN or DMSO containing a ruthenium complex (1.0×10^{-3} mol dm^{-3}) and a supporting electrolyte (R_4NBF_4, 0.1–0.05 mol dm^{-3}) under controlled potential electrolysis at −1.50 to −1.60 V (vs Ag/Ag^+). The electrolysis cell consisted of a glassy carbon working electrode (*ca* 2 cm^2), a magnesium ribbon auxiliary electrode, and an $Ag/AgNO_3$ reference electrode. At an appropriate interval of coulombs consumed in the reduction, a 0.1 cm^3 portion of gas was sampled from the gas phase with a pressure-locked syringe. Characterization and quantification of gaseous products was performed on a gas chromatograph. The analysis of the solution was carried out by sampling each 0.1 cm^3 portion from the DMSO solution at an appropriate interval of coulombs consumed. The amount of the formic acid was determined with an isotachophoretic analyzer. Quantitative analyses of CO and ketones produced in the electrolysis were conducted with a gas-mass and a gas chromatograph.

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