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Ruthenium Formyl Complexes as the Branch Point in Two- and Multi-Electron Reductions of CO_2

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There are a number of studies on electro-[1] and photochemical[2] CO_2 reductions affording CO and/or HCOOH by metal complexes. Recently, highly reduced products such as HCHO, CH_3OH, HOOCCHO, and $HOOCCH_2OH$, together with HCOOH and a small amount of CO, were obtained in electrochemical CO_2 reduction catalyzed by $[\mathrm{Ru(bpy)(trpy)(CO)}]^{2+}$ (bpy = 2,2′-bipyridine; trpy = 2,2′:6′,2″-terpyridine) in $EtOH/H_2O$ at −20 °C.[3] In this process, $[\mathrm{Ru(bpy)(trpy)(CHO)}]^+$, which results from two-electron reduction of $[\mathrm{Ru(bpy)(trpy)(CO)}]^{2+}$, functions as a key intermediate for the multi-electron reduction of CO_2. The fact that $[\mathrm{Ru(bpy)(trpy)(CO_2)}]$ is immediately converted to $[\mathrm{Ru(bpy)(trpy)(CO)}]^{2+}$ completely through $[\mathrm{Ru(bpy)(trpy)(C(O)OH)}]^+$ in protic media, however, has raised a question about the ratio of HCOOH to CO generation (1:0.015 at 100 C passed) in the CO_2 reduction catalyzed by $[\mathrm{Ru(bpy)(trpy)(CO)}]^{2+}$.[3] Taking into account the hydride donor ability of formyl complexes,[4−6] $[\mathrm{Ru(bpy)_2(CO)(CHO)}]^+$ may be a suitable model to elucidate the reactivity of $[\mathrm{Ru(bpy)(trpy)(CHO)}]^+$ as the key intermediate in the multi-electron reduction of CO_2, though $[\mathrm{Ru(bpy)_2(CO)(CHO)}]^+$ is not produced in the CO_2 reduction catalyzed by $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ due to a spontaneous Ru−CO bond cleavage of $[\mathrm{Ru(bpy)_2(CO)_2}]^0$.[7]

This communication reports the synthesis and reactivity of $[\mathrm{Ru(bpy)_2(CO)(CHO)}]^+$ as a mechanistic model of $[\mathrm{Ru(bpy)(trpy)(CHO)}]^+$.

Addition of a 1.5 molar excess of $NaBH_4$ to a colorless $MeOH/H_2O$ (2:1 v/v) solution of $[\mathrm{Ru(bpy)_2(CO)_2}](PF_6)_2$[7] at −5 °C resulted in gradual precipitation of yellow $[\mathrm{Ru(bpy)_2(CO)(CHO)}](PF_6)$ (**1**). The product was collected by filtration and washed with cold water. Yield: 75%. Anal. Found: C, 42.64; H, 2.85; N, 9.04. Calcd: C, 42.93; H, 2.76; N, 9.11. IR (KBr): ν(C=O) 1608 cm^{-1}, ν(C≡O) 1950 cm^{-1}. ^{1}H and ^{13}C NMR: δ 13.9, 265 (−CHO). The same reaction conducted in CH_3CN/H_2O (2:1 v/v) in place of $MeOH/H_2O$ selectively produced $[\mathrm{Ru(bpy)_2(CO)(CH_2OH)}](PF_6)$ (**2**) (80% yield)[3] without a precipitate of **1**. This result suggests smooth reduction of $[\mathrm{Ru(bpy)_2(CO)(CHO)}]^+$ to $[\mathrm{Ru(bpy)_2(CO)(CH_2OH)}]^+$ in protic media.

In contrast to the thermal stability of **2** in CH_3OH and CH_3CN, **1** slowly decomposed above −20 °C in those solvents. Thermal decomposition of **1** in CH_3OH at 0 °C gave $[\mathrm{Ru(bpy)_2(CO)(C(O)OCH_3)}](PF_6)$[7] (80% yield) (eq 1). Concomitant H_2

$$[\mathrm{Ru(bpy)_2(CO)(CHO)}]^+ + \mathrm{CH_3OH} \rightarrow [\mathrm{Ru(bpy)_2(CO)(C(O)OCH_3)}]^+ + \mathrm{H_2} \tag{1}$$

evolution (10% in 30 min) indicates that $[\mathrm{Ru(bpy)_2(CO)(C(O)OCH_3)}]^+$ is formed by the reaction of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ with CH_3O^-. On the other hand, a mixture of $[\mathrm{Ru(bpy)_2(CO)(CH_3CN)}](PF_6)_2$,[8] $[\mathrm{Ru(bpy)_2(CO)_2}](PF_6)_2$, and **2** was obtained upon warming a CH_3CN solution of **1** to ambient temperature. The formation of the last two, though the yield of **2** was 5%, implies hydride migration between two formyl complexes, presumably in the presence of contaminated water. Similar thermolysis of **1** in CO_2-saturated CH_3CN at 0 °C gave $HCOO^-$ (60% yield) with generation of $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ and a small amount of $[\mathrm{Ru(bpy)_2(CO)(CH_3CN)}]^{2+}$ (eq 2). It is worthy of note that

$$[\mathrm{Ru(bpy)_2(CO)(CHO)}]^+ + \mathrm{CO_2} \rightarrow [\mathrm{Ru(bpy)_2(CO)_2}]^{2+} + \mathrm{HCOO^-} \tag{2}$$

HCOOH formation in photo- and electrochemical CO_2 reductions catalyzed by $[\mathrm{Ru(bpy)_2(CO)H}]^+$ proceeds via $[\mathrm{Ru(bpy)_2(CO)(OC(O)H)}]^0$, which is formed by CO_2 insertion into the Ru−H bond of one-electron-reduced form of the hydride, and subsequently $HCOO^-$ is dissociated upon further one-electron reduction of $[\mathrm{Ru(bpy)_2(CO)(OC(O)H)}]^0$.[8] Thus $[\mathrm{Ru(bpy)_2(CO)H}]^+$, in contrast to **1**, does not react with CO_2 at room temperature without the electrochemical activation.

As a key intermediate in the first multi-electron reduction of CO_2 by $[\mathrm{Ru(bpy)(trpy)(CO)}]^{2+}$, $[\mathrm{Ru(bpy)(trpy)(CHO)}](PF_6)$ (**3**) was also obtained by a stoichiometric addition of $LiBEt_3H$ to a yellow CD_3CN solution of $[\mathrm{Ru(bpy)(trpy)(CO)}](PF_6)_2$ at −40 °C. The ^{1}H NMR spectra of the resulting violet solution revealed almost quantitative formation of **3** from a comparison

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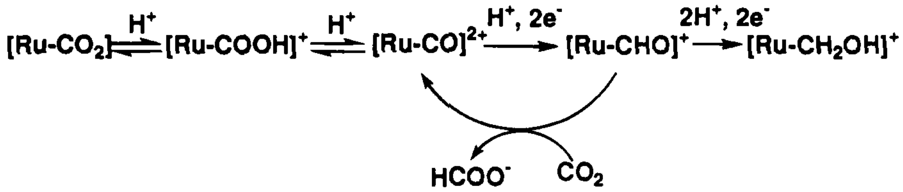
Scheme 1



of the signal intensities of the formyl proton at δ 13.8 and of the aromatic protons. An introduction of CO_2 into the violet solution by bubbling at that temperature resulted in a regeneration of a yellow $[Ru(bpy)(trpy)(CO)]^{2+}$ solution and $HCOO^-$ was generated in a 60% yield (eq 3). Thus, $HCOO^-$ is smoothly formed in the reaction of CO_2 with **1** and **3** without a redox reaction even at low temperature (eqs 2 and 3). Although only either formato (M−OC(O)H) or hydroxycarbonyl (M−C(O)-OH) species have been proposed as precursors for $HCOO^-$ formation in electro- and photochemical CO_2 reductions so far,[1i,7] the above results strongly indicate that formyl complexes are also possible intermediates for $HCOO^-$ formation.

$$[Ru(bpy)(trpy)(CHO)]^+ + CO_2 \rightarrow [Ru(bpy)(trpy)(CO)]^{2+} + HCOO^- \quad (3)$$

Scheme 1 represents a proposed pathway for multi-electron reduction of CO_2 *via* formyl and hydroxycarbonyl intermediates in protic media. Conversion from CO_2 to CO on metals can be explained by an acid−base equilibrium of metal−CO_2 adducts,[7] with CO evolution resulting from reduction of metal−carbonyl species. Formyl complexes are produced competitively by a two-electron reduction and protonation under similar conditions. Further reduction and protonation of the formyl complex produce a hydroxymethyl species which is a precursor to CH_3OH. In addition to undergoing further reduction, the formyl complex can react with CO_2, producing $HCOO^-$ with regeneration of metal carbonyl complexes, which are precursors for CO evolution. The presence of formyl intermediates (Scheme 1) as the branch point for two- and multi-electron reductions of CO_2 may, therefore, explain why most of the reduction products have been limited to CO and/or HCOOH in electro- and photochemical CO_2 reductions catalyzed by metal complexes reported so far.

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