APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 844–846 (2000)

NOTE

Characterization of $Ru(bpy)_2(CO)(COO)$ prepared by CO_2 addition to $Ru(bpy)_2(CO)$ in acetonitrile†

Etsuko Fujita,[1]* Mei Chou[1] and Koji Tanaka[2]
[1]Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000, USA
[2]Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

A carboxylate complex, $[Ru(bpy)_2(CO)(COO)]$, was prepared by the addition of CO_2 to the doubly reduced species, $[Ru^I(bpy)(bpy^{-\cdot})(CO)]$, in CH_3CN. The IR and UV–vis spectra of $[Ru(bpy)_2(CO)(COO)]$ show a marked cation and solvent dependence. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: carboxylates; carbon dioxide reduction; photocatalysis; small molecule activation; ruthenium

INTRODUCTION

Artificial photochemical CO_2 fixation has been extensively studied in the past two decades using various metal complexes.[1,2] Photochemical reduction of CO_2 has been achieved by using TEOA in DMF or the NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), in H_2O–DMF as quenchers in the presence of $Ru(bpy)_3{}^{2+}$ and $Ru(bpy)_2(CO)_2{}^{2+}$ under illumination at $\lambda > 400$ nm.[3–5] The system containing TEOA produces formate with a quantum yield of 0.14, whereas the system containing BNAH gives formate and CO with quantum yields of 0.03 and 0.15 respectively. Similar experiments with $Ru(bpy)_2(CO)(X)^{n+}$ ($X = Cl$, H, $n = 1$, or $X = CO$, $n = 2$) in TEOA–DMF are also reported to form formate from CO_2 with a maximum quantum yield of 15% with $Ru(bpy)_2(CO)(H)^+$.[6] The CO_2 reduction systems seem to involve a photochemical cycle for $Ru(bpy)_3{}^{2+}$ and a thermal cycle for $[Ru(bpy)_2(CO)X]^{n+}$. As shown in Eqns [1]–[5], the proposed mechanism involves reductive quenching of the $Ru(bpy)_3{}^{2+}$ excited state by TEOA to form $Ru(bpy)_3{}^+$, and reduction of $[Ru(bpy)_2(CO)X]^{n+}$ by two $Ru(bpy)_3{}^+$ molecules to produce $Ru(bpy)_2(CO)$. The latter was assumed to react with CO_2 to form $Ru(bpy)_2(CO)(COO)$ as a common intermediate for formate (Eqns [6] and [7] and CO (Eqns [4], [8], and [9]).

$$Ru(bpy)_3{}^{2+} + h\nu \rightarrow {}^*Ru(bpy)_3{}^{2+} \quad [1]$$

$${}^*Ru(bpy)_3{}^{2+} + TEOA \rightarrow Ru(bpy)_3{}^{+} + TEOA^+ \quad [2]$$

$$TEOA^+ + TEOA \rightarrow TEOAH^+ + (HOCH_2CH_2)_2NC^{\cdot}HCH_2OH \quad [3]$$

$$Ru(bpy)_2(CO)_2{}^{2+} + 2e^- \rightarrow Ru(bpy)_2(CO) + CO \quad [4]$$

$$e^- = Ru(bpy)_3{}^+ \text{ or } (HOCH_2CH_2)NC^{\cdot}HCH_2OH$$

$$Ru(bpy)_2(CO)X^+ + 2e^- \rightarrow Ru(bpy)_2(CO) + X^- \quad [5]$$

$$Ru(bpy)_2(CO) + CO_2 \rightarrow Ru(bpy)_2(CO)(COO) \quad [6]$$

$$Ru(bpy)_2(CO)(COO) + H^+ + 2e^- \rightarrow Ru(bpy)_2(CO) + HCOO^- \quad [7]$$

$Ru(bpy)_2(CO)(COO)$ and $[Ru(bpy)_2(CO)(COOH)]^+$ have been previously prepared by the addition of two and one equivalent of OH^- respectively to $[Ru(bpy)_2(CO)_2]^{2+}$ (Eqns. [8] and [9]) in aqueous solutions.[7] For the photochemical

---

* Correspondence to: Etsuko Fujita, Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000, USA.
E-mail: fujita@bnl.gov

† This note is based on work presented at the Fifth International Conference on Carbon Dioxide Utilization (ICCDU V), held on 5–10 September 1999 at Karlsruhe, Germany.

CO production, it is proposed that the reverse reactions are taking place to produce $Ru(bpy)_2(CO)_2{}^{2+}$ from $Ru(bpy)_2(CO)(COO)$, followed by the reduction of $Ru(bpy)_2(CO)_2{}^{2+}$ to form $Ru(bpy)_2(CO)$ and CO (Eqns. [6], [8], [9] and [4]). However, the electrochemical reduction of $[Ru(bpy)(CO)_2Cl_2]$ or $[Ru(bpy)_2(CO)_2]^{2+}$ in CH_3CN results in the formation of a polymeric film, $[Ru(bpy)(CO)_2]_n$, on the electrode surface instead of yielding the doubly reduced species, $Ru(bpy)_2(CO)$.[8,9]

$$Ru(bpy)_2(CO)_2{}^{2+} + OH^- \rightarrow Ru(bpy)_2(CO)(COOH)^+ \quad [8]$$

$$Ru(bpy)_2(CO)(COOH)^+ + OH^- \rightarrow Ru(bpy)_2(CO)(COO) + H_2O \quad [9]$$

These air-stable species, $[Ru(bpy)_2(CO)_2](PF_6)_2$, $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$ and $[Ru(bpy)_2(CO)(COOH)](CF_3SO_3)(H_2O)$ have been characterized by X-ray diffraction and various types of spectroscopy.[10–12] In order to elucidate the mechanism of photochemical CO_2 reduction in these systems, we have investigated the CO_2 binding to $Ru(bpy)_2(CO)$. Here we present an alternative preparation of $Ru(bpy)_2(CO)(COO)$ from $Ru(bpy)_2(CO)$, a doubly reduced species generated from $[Ru(bpy)_2(CO)Cl]^+$ in acetonitrile, and mechanistic aspects of CO_2 reduction in the photochemical system.

EXPERIMENTAL SECTION

The complexes $[Ru(bpy)(CO)_2](PF_6)_2$, $[Ru(bpy)_2(CO)Cl]PF_6$ were prepared as previously described and characterized by UV–vis and IR spectroscopies.[7,13,14] Acetonitrile and triethylamine (TEA) were purified using the published procedures and stored under vacuum over activated molecular sieves (3A) and sodium–potassium alloy (NaK) respectively.[15] Research-grade CO_2 ($CO_2 >$ 99.998%) was used without further purification. UV–vis and FTIR spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer and a Mattson Polaris FT-IR spectrometer respectively. Cyclic voltammograms in CH_3CN were obtained on a BAS100 electrochemical analyzer with scan rates ranging from 2 to 100 mV s^{-1} using a conventional H-type cell with solutions containing 1 mM ruthenium complex and 0.1 M tetrapropylammonium perchlorate in dry CH_3CN. Graphite, platinum and a standard calomel electrode (SCE) were used as working, counter and reference electrodes respectively. Ferrocene was used as an internal standard.

RESULTS AND DISCUSSION

Although the two-electron reduction wave in the cyclic voltammogram (CV) of $[Ru(bpy)_2(CO)_2]^{2+}$ in CH_3CN at -1.0 V (vs SCE) is not affected by CO_2, the second reduction wave of $[Ru(bpy)_2(CO)Cl]^+$ at -1.55 V indicates an increase in current under CO_2. A very intense blue color develops with reduction of $[Ru(bpy)_2(CO)_2]^{2+}$ by Na–Hg, which is indicative of a metal center reduction. The resulting solution does not react with CO_2. With or without CO_2, a black species is precipitated and the solution becomes almost colorless. The species is $[Ru(bpy)(CO)_2]_n$, produced by loss of a bpy ligand, as investigated by Ziessel and co-workers in the electrochemical CO_2 reduction using the ruthenium mono-and bis-bpy carbonyl species on an electrode surface.[8,9] Interestingly, both Tanaka's and Lehn's groups reported a decrease of catalytic activity with formation of a black precipitate during photoreduction of CO_2.[3–6] Therefore, the proposed mechanism of CO production from $[Ru(bpy)_2(CO)_2]^{2+}$ with two molecules of $Ru(bpy)_3{}^+$ serving as the electron source may not be involved in photochemical CO_2 reduction.

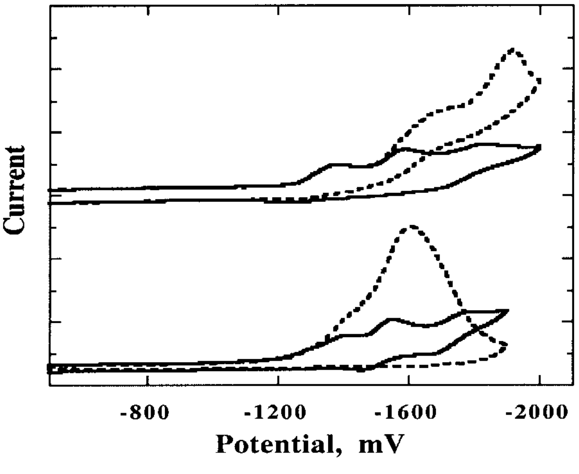

Figure 1 CV of $[Ru(bpy)_2(CO)Cl]^+$ in CH_3CN. Solid line: under Ar; dotted line: under CO_2; top: with Pr_4NClO_4; bottom: with $LiClO_4$.

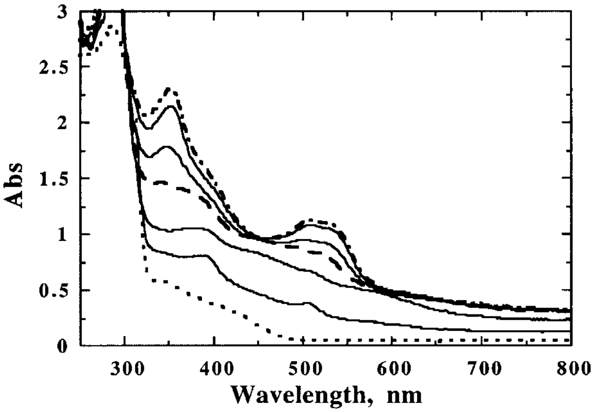

Figure 2 Spectral change of $[Ru(bpy)_2(CO)Cl]^+$ in CH_3CN during two electron reduction of $[Ru(bpy)_2(CO)Cl]^+$, ----- the mono-reduced species, – – – – – the di-reduced species.

The CV of $[Ru(bpy)_2(CO)Cl]^+$ indicates three reduction waves between −1.3 and −1.9 V, as shown in Fig. 1 by the solid line. The catalytic current observed under CO_2, shown by the dotted line, depends on the electrolytes present (top: Pr_4NClO_4; bottom: $LiClO_4$). The spectral change during two-electron reduction is shown in Fig. 2. The first reduction seems to be the bpy-centered reduction. Within a few minutes, two tiny peaks at 395 and 510 nm disappear, indicating that intramolecular electron transfer is taking place to form $[Ru^I(bpy)_2(CO)]$ with loss of a Cl^- ligand. The mono-reduced species does not react with CO_2. The second reduction is the formation of a ruthenium (I) bpy radical. Upon addition of CO_2, the color of the solution changes from reddish purple to brown with formation of the COO adduct exhibiting IR stretching bands at 1966, 1935, 1252 cm^{-1}. These stretching frequencies do not agree with published KBr data on $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$. Although the carboxylate, $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$, is not soluble in CH_3CN, the addition of salts causes its dissolution. In the presence of Li^+ or Na^+ the carboxylate is slowly converted to the carboxylic acid in CH_3CN, probably from a trace amount of water. Since Na–Hg was used to reduce $[Ru(bpy)_2(CO)Cl]^+$ in our experiments, the resulting solution contains Na^+ and the IR bands should correspond to those obtained with Na^+. In fact, two bands at 1935 and 1252 cm^{-1} are due to the carboxylate and a band at 1966 cm^{-1} is due to the carboxylic acid adduct.

IR and UV–vis spectra of $Ru(bpy)_2(CO)(COO)$ show a marked cation and solvent dependence. Upon the removal of water from the orange solid $[Ru(bpy)_2(CO)(COO)]\cdot 3H_2O$, the dark brown $Ru(bpy)_2(CO)(COO)$ forms and the C≡O stretching frequency shifts from 1911 to 1957 cm^{-1} (KBr). However, this species seems fairly unstable. Interaction between the cation (or solvent) and the bound CO_2 must enhance charge transfer from ruthenium and bpy to CO_2, and stabilize the CO_2 adduct as a stable ruthenium (II) carboxylate complex at room temperature and ambient pressures. Investigations of kinetics and mechanisms of photochemical reduction of CO_2 continue with $[Ru(bpy)_2(CO)(COO)]$ and $[Ru(bpy)_2(CO)H]^+$.

Acknowledgements The research at Brookhaven National Laboratory was carried out under contract DE-AC02-98CH10886 with the US Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

REFERENCES

1. Inui T, Anpo M, Izui K, Yanagida S, Yamaguchi T. In *Studies in Surface Science and Catalysis*, Delmon B, Yates JT (eds.). Elsevier: Amsterdam, 1998.
2. Halmann MM, Steinberg M. *Greenhouse Gas Carbon Dioxide Mitigation, Science and Technology*. Lewis Publishers: Boca Raton, FL, 1999.
3. Ishida H, Tanaka K, Tanaka T. *Chem. Lett.* 1988; 339–342.
4. Ishida H, Terada T, Tanaka K, Tanaka T. *Inorg. Chem.* 1990; **29**: 905–911.
5. Ishida H, Tanaka K, Tanaka T. *Organometallics* 1987; **6**: 181–186.
6. Lehn J-M, Ziessel R. *J. Organomet. Chem.* 1990; **382**: 157–173.
7. Ishida H, Tanaka K, Morimoto M, Tanaka T. *Organometallics* 1986; **5**: 724–730.
8. Chardon-Noblat S, Collomb-Dunand-Sauthier M-N, Deronzier A, Ziessel R, Zsoldos D. *Inorg. Chem.* 1994; **33**: 4410–4412.
9. Collomb-Dunand-Sauthier M-N, Deronzier A, Ziessel R. *J. Chem. Soc. Chem. Commun.* 1994; 189–191.
10. Tanaka H, Tzeng B-C, Nagao H, Peng S-M, Tanaka K. *Inorg. Chem.* 1993; **32**: 1508–1512.
11. Tanaka H, Nagao H, Peng S-M, Tanaka K. *Organometallics* 1992; **11**: 1450–1451.
12. Toyohara K, Nagao H, Adachi T, Yoshida T, Tanaka K. *Chem. Lett.* 1996; 27–28.
13. Kelly JM, O'Connel CM, Vos JG. *Inorg. Chim. Acta* 1982; **64**: L75–L76.
14. Clear JM, Kelly JM, O'Connel CM. *J. Chem. Soc. Chem. Commun.* 1980; 750–751.
15. Riddick JA, Bunger WB, Sakano TK. *Organic Solvents, Physical Properties and Methods of Purification*. Wiley: New York, 1986.