limitation might be removed in a enzymatic catalase using polynuclear active sites or binuclear sites acting cooperatively.

It is relevant to note that catalase activity is partly due to the relatively weak oxidizing properties of $Mn^{III,IV}$edda at pH >6. If $H_2O_2$ reduced $Mn^{III,IV}$edda easily (as does hydroxylamine), catalase activity would be nil since the trinuclear species derived from the mixed-valence complex via reaction 6 serves as the substrate for peroxide reduction. Other manganic catalases could form the same reactive intermediate(s) by other pathways. A possible test for the occurrence of steps similar to those in Schemes I and II in bacterial catalases would be inhibition or deactivation by reducing agents. Some published experiments on the *Lactobacillus* catalase seem to bear this out[29] though other factors such as loss of manganese might also be involved.

**Acknowledgment.** This work was supported by a grant from the Council for Tobacco Research Inc., U.S.A. Work done by J.D.R. while at Brookhaven National Laboratory was supported by NIH Grant RO1 GM23656-12. We wish to thank Drs. D. E. Cabelli at BNL for helpful discussions and assistance with pulse-radiolysis experiments and D. F. Church and B. Hales at LSU for assistance with ESR instrumentation.

---

(29) Kono, Y.; Fridovich, I. *J. Biol. Chem.* **1983**, *258*, 13647.

---

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

# Photochemical $CO_2$ Reduction Catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ Using Triethanolamine and 1-Benzyl-1,4-dihydronicotinamide as an Electron Donor

Hitoshi Ishida, Tohru Terada, Koji Tanaka,*,† and Toshio Tanaka

*Received July 29, 1988*

Irradiation with visible light of a $CO_2$-saturated triethanolamine (TEOA)/*N,N*-dimethylformamide (DMF) solution (1:4 v/v) containing $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2′-bipyridine) selectively produced $HCOO^-$ with a maximum quantum yield of 14%. On the other hand, the photochemical $CO_2$ reduction in $CO_2$-saturated $H_2O$/DMF (1:9 v/v) containing $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(CO)_2]^{2+}$, and 1-benzyl-1,4-dihydronicotinamide (BNAH) gave not only CO but also $HCOO^-$ with maximum quantum yields of 14.8 and 2.7%, respectively. In those photochemical $CO_2$ reductions, the luminescent-state $[Ru(bpy)_3]^{2+*}$ was quenched reductively by TEOA and BNAH, affording $[Ru(bpy)_3]^+$, which functioned as a reductant of $[Ru(bpy)_2(CO)_2]^{2+}$, and the change in the main product from $HCOO^-$ in TEOA/DMF to CO in $H_2O$/DMF can be explained in terms of the acid-base equilibria among $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(bpy)_2(CO)(C(O)OH)]^+$, and $[Ru(bpy)_2(CO)(COO^-)]^+$.

## Introduction

Interest in carbon dioxide fixation has increased recently because of its potential use as a $C_1$ source, the increase of its concentration in air, and efforts to mimic photosynthetic carbon assimilation.[1] Carbon dioxide is reduced at potentials more negative than −2.0 V vs SCE.[2] On the other hand, the reduction of $CO_2$ occurs at more positive potentials when protons are involved in the reduction. Reductions of $CO_2$ by means of various electrochemical,[3-14] photoelectrochemical,[15-18] and photochemical[19-28] methods have, therefore, been conducted in the presence of proton donors, where $CO_2$ is reduced to CO,[3,4,15,22-24,28] HCOOH,[5,6,16,17,19-21,27] HCHO,[18] $CH_3OH$,[7,11] $CH_4$,[12,13,25] and other organic compounds.[8,9] Another approach to $CO_2$ fixation is to activate or reduce organic molecules in order that they will react with $CO_2$, affording organic acids.[14,26] In such $CO_2$-fixation reactions, transition-metal catalysts,[3-10,19-25,27,28] semiconductor electrodes,[11,12,15,17,18] or enzymes[16,26] have been used for the activation of either $CO_2$ or organic molecules.

It is well-known that the reduced form of nicotinamide adenine dinucleotide phosphate (NAD(P)H) plays the role of a reductant in biological $CO_2$ fixation.[29] In this connection, electron transfer from NAD(P)H model compounds to various substrates has been studied extensively,[30] although no photochemical $CO_2$ reduction using NAD(P)H model compounds such as 1-benzyl-1,4-dihydronicotinamide (BNAH) has been reported. Among the transition-metal complexes used as catalysts in the photochemical $CO_2$ reduction,[19-26] $Re(bpy)(CO)_3Cl$ functions not only as a photosensitizer but also as a catalyst in $CO_2$ reduction.[22] On the other hand, there have been conflicting views with respect to the function of $[Ru(bpy)_3]^{2+}$ in the photochemical $CO_2$ reduction; an irradiation with light (λ > 320 nm) of a $CO_2$-saturated triethanolamine (TEOA)/DMF solution containing $[Ru(bpy)_3]^{2+}$ (0.06 mmol $dm^{-3}$) and methylviologen has been shown to produce $HCOO^-$.[19] It has, however, been reported that $HCOO^-$ formed

---

† Present address: Institute for Molecular Science, Okazaki National Research Institute, Myodaiji, Okazaki 444, Japan.

(1) Inoue, S., Yamazaki, N., Eds. *The Organic and Bioorganic Chemistry of Carbon Dioxide*; Halstead Press: New York, 1982. Friedli, H.; Lötscher, H.; Siegenthaler, U.; Stauffer, B. *Nature* **1986**, *324*, 237.

(2) Amatore, C.; Savéant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 5021.

(3) (a) Ishida, H.; Tanaka, K.; Tanaka, T. *Organometallics* **1987**, *6*, 181. (b) Ishida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1985**, 405.

(4) (a) DuBois, D. L.; Miedaner, A. *J. Am. Chem. Soc.* **1987**, *109*, 113. (b) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7461. (c) Pearce, D. J.; Plether, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *197*, 317. (d) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1414. (e) Bolinger, C. M.; Sullivan, B. P.; Conrad, D.; Gilbert, J. A.; Story, N.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1985**, 796. (f) Lieber, C. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1984**, *106*, 5033. (g) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328. (h) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1984**, 1315. (i) Fisher, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361.

(5) Ishida, H.; Tanaka, H.; Tanaka, K.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* **1987**, 131.

(6) (a) Nakazawa, M.; Mizobe, Y.; Matsumoto, Y.; Uchida, Y.; Tezuka, M.; Hidai, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 809. (b) Slater, S.; Wagenknecht, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5367. (c) Stalder, C. J.; Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 3673. (d) Kapusta, S.; Hackerman, N. *J. Electrochem. Soc.* **1984**, *131*, 1511. (e) Takahashi, K.; Hiratsuka, K.; Sasaki, H.; Toshima, S. *Chem. Lett.* **1979**, 305.

(7) Ogura, K.; Takamagari, K. *J. Chem. Soc., Dalton Trans.* **1986**, 1519.

(8) Ishida, H.; Tanaka, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1987**, 597.

(9) (a) Becker, J. Y.; Vainas, B.; Eger, R.; Kaufman, L. *J. Chem. Soc., Chem. Commun.* **1985**, 1471. (b) Tezuka, M.; Yajima, T.; Tsuchiya, A.; Matsumoto, Y.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1982**, *104*, 6834.

(10) (a) Hiratsuka, K.; Takahashi, K.; Sasaki, H.; Toshima, S. *Chem. Lett.* **1977**, 1137. (b) Meshitsuka, S.; Ichikawa, M.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1974**, 158.

(11) (a) Frese, K. W., Jr.; Canfield, D. *J. Electrochem. Soc.* **1984**, *131*, 2518. (b) Canfield, D.; Frese, K. W., Jr. *J. Electrochem. Soc.* **1983**, *130*, 1772.

(12) Frese, K. W., Jr.; Leach, S. *J. Electrochem. Soc.* **1985**, *132*, 259.

(13) Hori, Y.; Kikuchi, K.; Murata, A.; Suzuki, S. *Chem. Lett.* **1986**, 897.

0020-1669/90/1329-0905$02.50/0 © 1990 American Chemical Society

in the presence of low (0.06 mmol $dm^{-3}$) and high (11 mmol $dm^{-3}$) concentrations of $[Ru(bpy)_3]^{2+}$ in TEOA/DMF under photoirradiation comes from TEOA[31] and $CO_2$,[20] respectively. On the basis of the fact that most of photochemical $CO_2$ reductions have been conducted in the presence of $[Ru(bpy)_3]^{2+}$[19-21,23,24,26] and its derivative,[25] it is very important to clarify the function of $[Ru(bpy)_3]^{2+}$ in the photochemical $CO_2$ reduction. This paper describes the photochemical $CO_2$ reduction catalyzed by the system composed of $[RuL_3]^{2+}$ and $[RuL_2(CO)_2]^{2+}$ (L = bpy, 1,10-phenanthroline) in the presence of TEOA[27] or BNAH[28] in DMF or in $H_2O$/DMF and the functions of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ in the catalytic cycle.

## Experimental Section

**Material.** The preparations of $[Ru(bpy)_2(CO)_2](PF_6)$,[32] $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$,[33] $[Ru(phen)_3](PF_6)_2$,[34] and $Ru(bpy)_2Cl_2 \cdot 2H_2O$[35] were described elsewhere. *N*,*N*-Dimethylformamide (DMF) was purified by azeotropic distillation with benzene, followed by distillation under reduced pressure, and stored under an $N_2$ atmosphere. Triethanolamine (TEOA), DMF-$d_7$, $Na_2{}^{13}CO_3$, and $H^{13}COONa$ were purchased from Wako Pure Chemicals and used without further purification. 1-Benzyl-1,4-dihydronicotinamide (BNAH) prepared according to the literature[36] was purified by recrystallization from ethanol and stored under $N_2$ in a refrigerator. Potassium ferrioxalate[37] used as an actinometer was purified by recrystallization from hot water.

**Table I.** Photochemical $CO_2$ Reduction in $CO_2$-Saturated TEOA/DMF (1:4 v/v, 5 $cm^3$) under Irradiation with Light ($\lambda > 320$ nm; 300-W Hg Lamp) for 20 h

| | concn, mmol $dm^{-3}$ | | | |
|---|---|---|---|---|
| entry | $[Ru(bpy)_3]^{2+}$ | $[Ru(phen)_3]^{2+}$ | $[Ru(bpy)_2(CO)_2]^{2+}$ | μmol of $HCOO^-$ |
| 1 | 0.50 | | | 7 |
| 2 | | | 0.50 | 0 |
| 3 | 0.50 | | 0.01 | 186 |
| 4 | 0.50 | | 0.05 | 258 |
| 5 | 0.50 | | 0.10 | 315 |
| 6 | 0.50 | | 0.50 | 394 |
| 7 | 0.50 | | 1.00 | 324 |
| 8 | 0.50 | | 1.50 | 265 |
| 9 | 0.50 | | 2.00 | 265 |
| 10 | 0.50 | | 0.50[a] | 193 |
| 11 | | 0.50 | | 7 |
| 12 | | 0.50 | 0.25 | 117 |
| 13 | | 0.50 | 0.50 | 139 |
| 14 | | 0.50 | 0.75 | 150 |
| 15 | | 0.50 | 1.00 | 118 |
| 16 | | 0.50 | 1.50 | 114 |
| 17 | | 0.50 | 2.00 | 89 |
| 18[b] | 0.50 | | | 0 |
| 19[b] | 0.50 | | 0.50 | 93 |
| 20[b] | | | 0.50 | 0 |
| 21[b] | 0.50 | | 0.10[c] | 73 |

[a] $Ru(bpy)_2Cl_2$ was used in place of $[Ru(bpy)_2(CO)_2]^{2+}$. [b] In TEOA/$CH_3CN$ (1:4 v/v). [c] $[Ru(phen)_2(CO)_2]^{2+}$ was used in place of $[Ru(bpy)_2(CO)_2]^{2+}$.

**Preparation of $[Ru(phen)_2(CO)_2](PF_6)_2$.** A 90% formic acid solution (50 $cm^3$) of $RuCl_3 \cdot nH_2O$ (1.0 g) was refluxed under $N_2$ for 5 h. The resulting clear orange solution was cooled to room temperature and evaporated to dryness under reduced pressure to afford an orange solid, which was dissolved in an $H_2O$/EtOH (1:4 v/v) solution of 1,10-phenanthroline (1.0 g, 5.5 mmol). The solution was refluxed under $N_2$ for 2 h, followed by cooling to 273 K to give $Ru(phen)_2Cl_2$ as an orange precipitate. A mixture of $Ru(phen)_2Cl_2$ thus obtained and 1,10-phenanthroline (1.0 g, 5.5 mmol) in $H_2O$/EtOH (2:1 v/v, 100 $cm^3$) was heated under refluxing conditions for 24 h. Addition of concentrated aqueous $NH_4PF_6$ to the solution at room temperature yielded an off-white precipitate, which was purified by recrystallization from acetone/ether, 78% yield. Anal. Calcd for $C_{26}H_{16}F_{12}N_4O_2P_2Ru$: C, 38.65; H, 2.00; N, 6.93. Found: C, 38.73; H, 2.13; N, 7.08. Mp 285 °C dec; IR (KBr) $\nu$(CO) 2048, 2100 $cm^{-1}$; $^1H$ NMR ($CD_3CN$) $\delta$ 7.51 (d, 4 H), 8.00–8.29 (6 H), 8.56 (t, 2 H), 8.94 (d, 2 H), 9.43 (d, 2 H); UV–visible ($CH_3CN$) $\lambda_{max}$ 351 (log $\epsilon$ 3.56), 336 (3.58), 272 (4.76), 224 nm (4.82).

**Photochemical $CO_2$ Reduction.** Carbon dioxide was bubbled for 30 min through a Teflon tube into a TEOA/DMF (1:4 v/v) solution (5 $cm^3$) containing fixed amounts of $[Ru(bpy)_3]Cl_2$ and $[Ru(bpy)_2(CO)_2](PF_6)_2$. The solution was contained in a Pyrex tube (32 $cm^3$), and the Teflon tube was inserted through a septum cap. The photochemical $CO_2$ reduction was conducted under irradiation with light (300-W Hg lamp) through a cutoff chemical filter (1 cm) prepared by 0.50 mol $dm^{-3}$ of $CuSO_4$ ($\lambda < 320$ nm). The photochemical $CO_2$ reduction using BNAH as an electron donor was similarly conducted in $H_2O$/DMF (1:9 or 3:7 v/v) containing fixed amounts of $[Ru(bpy)_3]Cl_2$, $[Ru(bpy)_2(CO)_2](PF_6)_2$, and BNAH under irradiation with light through a cutoff chemical filter (1 cm) of 0.5 mol $dm^{-3}$ of $NaNO_2$ ($\lambda < 400$ nm). After the lapse of a fixed time, 0.1-$cm^3$ portions of gas and the solution were sampled from the gaseous and liquid phases in the flask through the septum cap with syringe techniques. Quantitative analysis of the gas was performed on a Shimadzu GC-3BT gas chromatograph with a 2-m column filled with 13X molecular sieves at 343 K using He (40 $cm^3$/min) as a carrier gas. The amount of $HCOO^-$ formed in the solution was determined with a Shimadzu IP-2A isotachophoretic analyzer using a mixture of $\beta$-alanine (0.02 mol $dm^{-3}$) and HCl (0.01 mol $dm^{-3}$) in an aqueous Triton X-100 (0.2 vol %) solution and caproic acid (0.01 mol $dm^{-3}$) in $H_2O$ as leading and terminal electrolytes, respectively.

---

(14) (a) Tanaka, K.; Matsui, T.; Tanaka, K. *J. Am. Chem. Soc.* **1989**, *111*, 3062. (b) Tanaka, K.; Wakita, R.; Tanaka, T. *J. Am. Chem. Soc.* **1989**, *111*, 2428. (c) Silvestri, G.; Gambino, S.; Filardo, G. *Tetrahedron Lett.* **1986**, *27*, 3429. (d) Torii, S.; Tanaka, H.; Hamatani, T.; Morisaki, K.; Jutand, A.; Pfluger, F.; Fauvarque, J.-F. *Chem. Lett.* **1986**, 169. (e) Sock, O.; Troupel, M.; Perichon, J. *Tetrahedron Lett.* **1985**, *26*, 1509. (f) Silvestri, G.; Gambino, S.; Filardo, G.; Greco, G.; Gluotta, A. *Tetrahedron Lett.* **1984**, *25*, 4307.

(15) Bradley, M. G.; Tysak, T.; Graves, D. J.; Valchopoulos, N. A. *J. Chem. Soc., Chem. Commun.* **1983**, 349.

(16) Parkinson, B.; Weaver, P. *Nature* **1984**, *309*, 148.

(17) Ikeda, S.; Yoshida, M.; Ito, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1353.

(18) (a) Sears, W. M.; Morrison, S. R. *J. Phys. Chem.* **1985**, *89*, 3295. (b) Ito, K.; Ikeda, S.; Yoshida, M.; Ohta, S.; Iida, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 583. (c) Taniguchi, Y.; Yoneyama, H.; Tamura, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2034. (d) Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. *Nature* **1979**, *277*, 637.

(19) Kitamura, N.; Tazuke, S. *Chem. Lett.* **1983**, 1109.

(20) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 56.

(21) Mandler, D.; Willner, I. *J. Am. Chem. Soc.* **1987**, *109*, 7884.

(22) (a) Kutal, C.; Corbin, A. J.; Ferraudi, G. *Organometallics* **1987**, *6*, 553. (b) Hawecher, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990. (c) Kutal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. *Organometallics* **1985**, *4*, 2161. (d) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536.

(23) (a) Ziessel, R.; Hawecker, J.; Lehn, J.-M. *Helv. Chim. Acta* **1986**, *69*, 1065. (b) Lehn, J.-M.; Ziessel, R. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 701.

(24) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2105.

(25) (a) Maidan, R.; Willner, I. *J. Am. Chem. Soc.* **1986**, *108*, 8100. (b) Wilner, I.; Maidan, R.; Mandler, D.; Durr, H.; Dorr, G.; Zengerle, K. *J. Am. Chem. Soc.* **1987**, *109*, 6080.

(26) Willner, I.; Mandler, D.; Riklin, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1022.

(27) Ishida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1987**, 1035.

(28) Ishida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1988**, 339.

(29) Arnon, D. I. In *Bioorganic Chemistry IV*; van Tamelen, E. E., Ed.; Academic Press: New York, 1978; p 4.

(30) (a) Fukuzumi, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1983**, *105*, 4722. (b) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305 and references therein.

(31) Kase, H.; Iida, T.; Yamane, K.; Mitamura, T. *Denki Kagaku* **1986**, *54*, 437.

(32) Ishida, H.; Tanaka, K.; Morimoto, M.; Tanaka, T. *Organometallics* **1986**, *5*, 724.

(33) Burstall, F. H. *J. Chem. Soc.* **1936**, 173.

(34) (a) Lin, C.-T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536. (b) Mercer, E. E.; Buckley, R. R. *Inorg. Chem.* **1965**, *4*, 1692.

(35) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(36) Anderson, A. G., Jr.; Berkelhammer, G. *J. Am. Chem. Soc.* **1958**, *80*, 992.

(37) (a) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518. (b) Calvert, J. G.; Parker, J. N. *Photochemistry*; Wiley: New York, 1966; p 783.

$^{13}$C NMR experiments were performed in a DMF-$d_7$/DMF/TEOA (5:3:2 v/v, 1.0 cm$^3$) solution containing an equal amount of $[Ru(bpy)_3]Cl_2$ and $[Ru(bpy)_2(CO)_2](PF_6)_2$ ($5.0 \times 10^{-4}$ mol dm$^{-3}$) in a NMR tube (i.d. 1.0 cm). The tube was thoroughly flushed with He by means of a Teflon tube in order to remove air, and then $^{13}CO_2$ prepared by addition of $H_2SO_4$ (0.10 N) to an aqueous solution of 99% $Na_2{}^{13}CO_3$ (1.0 g) was bubbled into the solution through a glass tube packed with $CaCl_2$. After photoirradiation for 20 h, the $^{13}$C NMR spectra of the solutions were obtained at 15.3 MHz with a JEOL EX-60 spectrometer against TMS as the internal standard. Oxidation products of BNAH were determined as 4,4′- and 4,6′-linked BNA dimers[38] by HPLC and $^1$H NMR and electronic spectroscopy. HPLC analysis was carried out with a JASCO 880-PU instrument equipped with a 20-cm column filled with JASCO Finepack SIL C18 sorbent using $MeOH/H_2O$ (3:2 v/v) as an eluent. The effluent was monitored at 355 nm by use of a JASCO 875-UV spectrophotometer. $^1$H NMR spectra were recorded on a JEOL-PS-100 spectrometer. Electronic absorption spectra were measured with an Union SM-401 spectrophotometer.

**Quantum Yield Determination.** The quantum yield of the photochemical $CO_2$ reduction was determined in a square quartz cuvette (1.0 cm). After $CO_2$ was bubbled into the test solution in the quartz cuvette (1.0 cm$^3$) with a Teflon tube for 30 min, the solution was irradiated with a 300-W Xenon lamp (Ushio Model U1-501) through a Toshiba Y-43 glass filter transmitting light ($\lambda > 400$ nm) for 5, 10, and 15 min. The rate of the photochemical $CO_2$ reduction was determined by analyses of CO and $HCOO^-$ formed in the gaseous and liquid phases, respectively. Potassium ferrioxalate was used as a standard actinometer for the determination of the quantum yield in the photochemical $CO_2$ reductions.[30a]

**Quenching Experiment of the Luminescence State of $[Ru(bpy)_3]^{2+*}$.** The relative emission intensities at 610 nm of $[Ru(bpy)_3]^{2+*}$ were determined by irradiation with light at 450 nm of an $O_2$-free DMF solution containing $[Ru(bpy)_3]Cl_2$ ($2.5 \times 10^{-4}$ mol dm$^{-3}$) and various amounts of TEOA or BNAH as a quencher with a Hitachi 650-10S fluorescence spectrophotometer. The Stern–Volmer relationship (eq 1) was obtained

$$I_0/I = 1 + k_q\tau[Q] \qquad (1)$$

between the concentration of the quencher (Q) and the relative emission intensity ($I_0/I$), where $I_0$ and $I$ represent the intensity at 610 nm in the absence and the presence of a quencher, respectively. The quenching rate constant $k_q$ ($=K_q\tau^{-1}$) was determined from the Stern–Volmer constant $K_q$ and the emission lifetime $\tau$ ($[Ru(bpy)_3]^{2+*}$, 930 ns in DMF).[39]

## Results and Discussion

**Photochemical $CO_2$ Reduction Using TEOA as an Electron Donor.** It has been reported that $[Ru(bpy)_3]^{2+}$ reduces $CO_2$ in TEOA/DMF (1:4 v/v) to afford $HCOO^-$ under irradiation with light ($\lambda > 400$ nm), while $[Ru(phen)_3]^{2+}$ has no ability to catalyze the photochemical $CO_2$ reduction under the same conditions.[20] On the other hand, irradiation with light ($\lambda > 320$ nm)[40] of $CO_2$-saturated TEOA/DMF (1:4 v/v) solutions (5 cm$^3$) of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ (0.50 mmol dm$^{-3}$) produced 7 and 5 $\mu$mol of $HCOO^-$, respectively, for 20 h (entries 1 and 11 in Table I). Although no photochemical $CO_2$ reduction took place in the presence of $[Ru(bpy)_2(CO)_2]^{2+}$ in TEOA/DMF (entry 2 in Table I), the coexistence of $[Ru(bpy)_3]^{2-}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ led to a drastic increase in the amount of $HCOO^-$ formed, which increased with increasing concentrations of $[Ru(bpy)_2(CO)_2]^{2+}$ (entries 3–6 in Table I) and reached the maximum value of 394 $\mu$mol when the concentration of $[Ru(bpy)_2(CO)_2]^{2+}$ was the same as that of $[Ru(bpy)_3]^{2+}$ (0.50 mmol dm$^{-3}$) (entry 6 in Table I). A further increase of the $[Ru(bpy)_2(CO)_2]^{2+}$ concentration, however, resulted in a gradual decrease in the formation of $HCOO^-$ (entries 7–10 in Table I). On the basis of the amount of $HCOO^-$, the catalytic activity of the system composed of $[Ru(phen)_3]^{2+}$ and $[Ru(bpy)_3(CO)_2]^{2+}$ is a fair degree lower than that of the $[Ru(bpy)_3]^{2+}/[Ru(bpy)_2(CO)_2]^{2+}$ system although the tendency for the amounts of $HCOO^-$ to depend on the mole ratios of $[Ru(bpy)_2(CO)_2]^{2+}$ to $[RuL_3]^{2+}$ (L = bpy, phen) is essentially consistent for both systems (compare entries 3–9 with those of 12–17 in Table I).

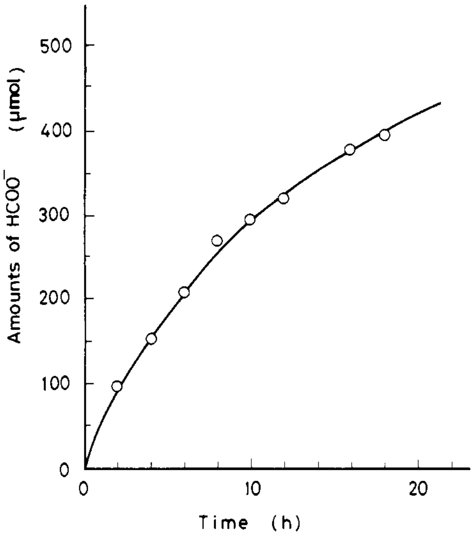


Figure 1. Plot of $HCOO^-$ formed vs irradiation time in the photochemical $CO_2$ reduction in $CO_2$-saturated TEOA/DMF (1:4 v/v) containing equimolar amounts of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ (0.50 mmol dm$^{-3}$), with $\lambda > 320$ nm.

In contrast to the photochemical $CO_2$ reduction in TEOA/DMF, neither $[Ru(bpy)_2(CO)_2]^{2+}$ nor $[Ru(bpy)_3]^{2+}$ had the ability to catalyze $CO_2$ reduction in TEOA/$CH_3CN$ (1:4 v/v) (entries 18 and 20 in Table I). Nevertheless, the coexistence of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ or $[Ru(phen)_2(CO)_2]^{2+}$ in the same medium also produced $HCOO^-$ catalytically (entries 19 and 21 in Table I). These results clearly indicate that $[RuL_3]^{2+}$ (L = bpy, phen) alone is unable to catalyze photochemical $CO_2$ reduction. In this connection, $HCOO^-$ generated in $CO_2$-saturated TEOA/DMF containing $[Ru(bpy)_3]^{2+}$ and $MV^{2+}$ under irradiation with light ($\lambda > 320$ nm) has been suggested to come from the decomposition of TEOA.[31] In order to clarify the carbon source of $HCOO^-$ formed in the present study, the photochemical $^{13}CO_2$ reduction was conducted in a DMF-$d_7$/DMF/TEOA (5:3:2 v/v) solution containing an equal amount of $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ (0.50 mmol dm$^{-3}$). The $^{13}$C NMR spectrum of the reaction mixture obtained after irradiation with light ($\lambda > 320$ nm) for 20 h clearly showed the formation of $H^{13}COO^-$ ($\delta$ 168.1 ppm) together with hydroxyacetaldehyde ($\delta$ 93.0 ppm) and diethanolamine ($\delta$ 60.1 ppm) as decomposition products of TEOA. In addition, the amount of $H^{13}COO^-$ determined by the $^{13}$C NMR signal intensity was consistent with that determined by an isotachophoretic analyzer. Thus, the catalytic system composed of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ can reduce $CO_2$ to afford $HCOO^-$ selectively under photoirradiation in TEOA/DMF. The observation of the drastic increase in $HCOO^-$ upon the addition of $[Ru(bpy)_2(CO)_2]^{2+}$ to a TEOA/DMF or TEOA/$CH_3CN$ solution of $[Ru(bpy)_3]^{2+}$ suggests that a small amount of $HCOO^-$ formed in the absence of $[Ru(bpy)_2(CO)_2]^{2+}$ (entries 1 and 11 in Table I) was generated by a trace amount of bis(bipyridine)ruthenium species, in addition to $[Ru(bpy)_3]^{2+}$, maybe resulting from a dissociation of a bpy ligand from $[Ru(bpy)_3]^{2+}$ under photoirradiation, as suggested previously.[20] In fact, the photochemical $CO_2$ reduction in the presence of an equimolar amount of $[Ru(bpy)_3]^{2+}$ and $Ru(bpy)_2Cl_2$ (0.50 mmol dm$^{-3}$) produced 193 $\mu$mol of $HCOO^-$ in TEOA/DMF (1:4 v/v) for 20 h (entry 10 in Table I). This result indicates that the coexistence of $[RuL_3]^{2+}$ (L = bpy, phen) and $RuL_2$ species having labile ligands such as CO and Cl is endowed with the ability to catalyze photochemical $CO_2$ reduction.

A plot of the amount of $HCOO^-$ formed under the optimum conditions (entry 6 in Table I) displays a gradual decrease of the reaction rate with time (Figure 1); a black precipitate slowly appeared during the photochemical $CO_2$ reduction. The decrease of the rate of formation of $HCOO^-$ with the lapse of time (Figure 1) may, therefore, have been caused not only by the decomposition

---

[38] Ohnishi, Y.; Kitami, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2674.

[39] Pac, C.; Miyauchi, Y.; Ishitani, O.; Ihama, M.; Yasuda, M.; Sakurai, H. *J. Org. Chem.* **1984**, *49*, 26.

[40] No difference was observed in the amounts of $HCOO^-$ formed in the photochemical $CO_2$ reduction in DMF/TEOA (4:1 v/v) containing $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ under irradiation with light at wavelengths above 320 nm and above 400 nm (entries 1–10 in Table I).

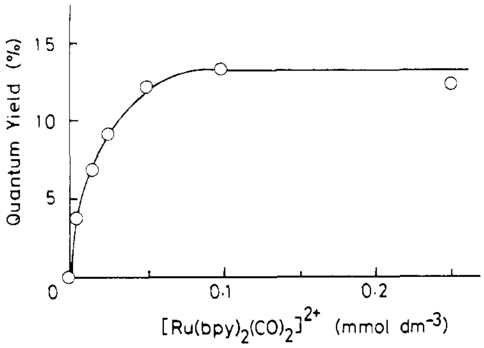


**Figure 2.** Quantum yield for the formation of $HCOO^-$ in the presence of various amounts of $[Ru(bpy)_2(CO)_2]^{2+}$ and at a constant concentration of $[Ru(bpy)_3]^{2+}$ (0.50 mmol $dm^{-3}$) in $CO_2$-saturated TEOA/DMF (1:4 v/v).

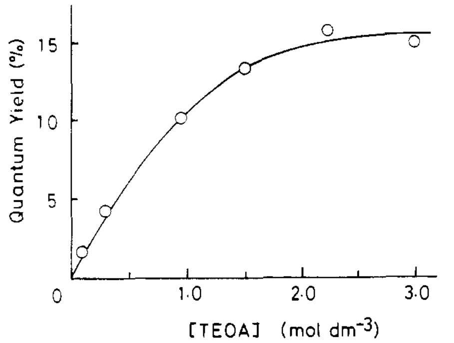


**Figure 3.** Quantum yield for the formation of $HCOO^-$ in the presence of various concentrations of TEOA and at constant concentrations of $[Ru(bpy)_3]^{2+}$ (0.5 mmol $dm^{-3}$) and $[Ru(bpy)_2(CO)_2]^{2+}$ (0.10 mmol $dm^{-3}$) in $CO_2$-saturated DMF.

of the catalyst but also by the filtering effects due to the dispersion of black solid in the solution. The quantum yield calculated from the amount of $HCOO^-$ formed in the initial 15 min, in which time no decomposition of the catalyst takes place, increased with increasing concentration of $[Ru(bpy)_2(CO)_2]^{2+}$ up to 0.10 mmol $dm^{-3}$, while the concentration of $[Ru(bpy)_3]^{2+}$ is held constant (0.50 mmol $dm^{-3}$) in TEOA/DMF (1:4 v/v), and reached the constant value of 14% above that concentration (Figure 2). This result indicates that 0.2 mol of $[Ru(bpy)_2(CO)_2]^{2+}$ to 1 mol of $[Ru(bpy)_3]^{2+}$ sufficed for the photochemical $CO_2$ reduction. On the other hand, the equimolar mixture of $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ gave the maximum yield for the formation of $HCOO^-$ (entry 6 in Table I). This discrepancy resulted from the gradual decrease of the catalytic activity of the $[Ru(bpy)_3]^{2+}$/$[Ru(bpy)_2(CO)_2]^{2+}$ system with time (Figure 1). The fact that the absorptivity at 450 nm of $[Ru(bpy)_3]^{2+}$ in the solution was essentially unchanged before and after the photochemical $CO_2$ reduction indicates that the black precipitate which appeared during photoirradiation results from the decomposition of $[Ru(bpy)_2(CO)_2]^{2+}$.

The concentration of TEOA also greatly influenced the quantum yield for the formation of $HCOO^-$; the value increased with increasing the TEOA concentration up to 2.0 mol $dm^{-3}$ in the presence of constant concentrations of $[Ru(bpy)_2(CO)_2]^{2+}$ (0.10 mmol $dm^{-3}$) and $[Ru(bpy)_3]^{2+}$ (0.50 mmol $dm^{-3}$) and reached the limiting value of 14% (Figure 3), similar to the limiting value obtained in Figure 2. The limiting quantum yield in the present study was almost the same as the value in the photochemical $CO_2$ reduction catalyzed by $Re(bpy)(CO)_3Cl$ in TEOA/DMF, where $CO_2$ was selectively reduced to CO. It is worth noting that photochemical reactions in TEOA/DMF were also influenced by the presence of $H_2O$; the photochemical $CO_2$ reduction in $CO_2$-saturated TEOA/DMF (1:4 v/v) containing $[Ru(bpy)_2(CO)_2]^{2+}$ (0.10 mmol $dm^{-3}$) and $[Ru(bpy)_3]^{2+}$ (0.50 mmol $dm^{-3}$) afforded 315 μmol of $HCOO^-$ (entry 5 in Table I), whereas the amount was decreased to 209 μmol in the same $CO_2$ reduction conducted in $CO_2$-saturated $H_2O$/TEOA/DMF (1:2:7 v/v) under otherwise the same conditions.[41] The decrease of the amount of $HCOO^-$ in the presence of $H_2O$ can be attributed to the decrease of the basicity of TEOA due to the protonation equilibrium ($pK_a = 7.9$)[42] (eq 2). Thus a basic molecule such as TEOA is not suitable as an electron donor in aqueous conditions.

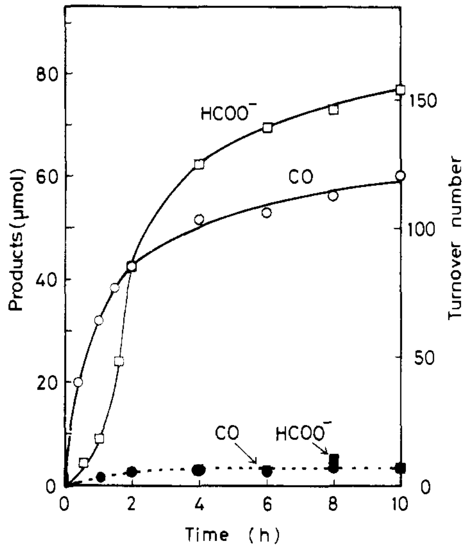


**Figure 4.** Photochemical $CO_2$ reduction in the presence of $[Ru(bpy)_3]^{2+}$ (0.50 mmol $dm^{-3}$), $[Ru(bpy)_2(CO)_2]^{2+}$ (0.10 mmol $dm^{-3}$), and BNAH (0.10 mol $dm^{-3}$) in $CO_2$-saturated dry DMF (a) and in $CO_2$-saturated $H_2O$/DMF (1:9 v/v) (b), with $\lambda > 400$ nm.

$$(HOCH_2CH_2)_3N + H^+ \rightleftharpoons (HOCH_2CH_2)_3NH^+ \quad (2)$$

**Photochemical $CO_2$ Reduction Using BNAH.** The photochemical $CO_2$ reduction using BNAH as an NAD(P)H model in an aqueous medium is of much interest from the point of view of the function of NAD(P)H in biological $CO_2$ fixation. Irradiation with visible light ($\lambda > 400$ nm)[43] of a $CO_2$-saturated dry DMF solution[44] containing $[Ru(bpy)_2(CO)_2]^{2+}$ (0.10 mmol $dm^{-3}$), $[Ru(bpy)_3]^{2+}$ (0.50 mmol $dm^{-3}$), and BNAH (0.10 mol $dm^{-3}$) resulted in a black precipitate, and trace amounts of $HCOO^-$ and CO were formed (the dotted line in Figure 4). On the other hand, photochemical $CO_2$ reduction under the same conditions but in $CO_2$-saturated $H_2O$/DMF (1:9 v/v) catalytically produced CO and $HCOO^-$ (compare solid and dotted lines in Figure 4) without forming a black precipitate. It should be noticed that not only $HCOO^-$ but also CO is formed in the photochemical $CO_2$ reduction in $H_2O$/DMF in contrast to the selective formation of $HCOO^-$ in TEOA/DMF (Figure 1).[45] Thus, $H_2O$ played the role of a proton source for the formation of CO and $HCOO^-$ in the photochemical $CO_2$ reduction and protected $[Ru(bpy)_2(CO)_2]^{2+}$ from decomposition caused by photoirradiation. As depicted in Figure 4, CO is produced as the main product in the initial stage. The rate of the formation, however, decreased rapidly after 2 h, and $HCOO^-$ became the main product. Such a change in the main product from CO to $HCOO^-$ in the photochemical $CO_2$ reduction in $H_2O$/DMF (1:9 v/v) was not caused by the decomposition of the catalyst system, since the rate of formation

---

(41) The yield of $HCOO^-$ in the photochemical $CO_2$ reduction in TEOA/DMF has been shown to decrease even in the presence of 2% $H_2O$.[20]

(42) Charlot, G.; TrèMillon, B. *Chemical Reactions in Solvents and Melts*; Pergamon Press: New York, 1969.

(43) BNAH absorbs light around the wavelength 320 nm and is exited to BNAH* with the lifetime $\tau = 1.7$ ns.[30b] However, BNAH* does not assist the present photochemical $CO_2$ reduction, since the amounts of CO and $HCOO^-$ formed in the irradiation with light ($\lambda > 320$ nm) of $CO_2$-saturated $H_2O$/DMF containing $[Ru(bpy)_2(CO)_2]^{2+}$ and BNAH was decreased to 80–90% compared with those formed under illumination with light ($\lambda > 400$ nm) of the same solution.

(44) This solution contains at least 3.0 mmol $dm^{-3}$ of $H_2O$ arising from $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (0.50 mmol $dm^{-3}$).

(45) A trace amount of CO (60–80% based on the amount of $[Ru(bpy)_2(CO)_2]^{2+}$) was confirmed in the gaseous phase in the photochemical $CO_2$ reduction in TEOA/DMF (1:4, 3:7 v/v).

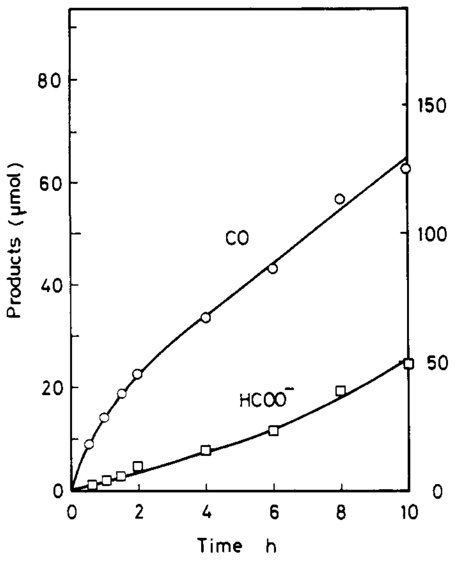


**Figure 5.** The photochemical $CO_2$ reduction in the presence of $[Ru(bpy)_3]^{2+}$ (0.50 mmol dm$^{-3}$), $[Ru(bpy)_2(CO)_2]^{2+}$ (0.10 mmol dm$^{-3}$), and BNAH (0.10 mol dm$^{-3}$) in $CO_2$-saturated $H_2O$/DMF (3:7 v/v), with $\lambda > 400$ nm.

of not only CO but also $HCOO^-$ was essentially unchanged for 10 h in the photochemical $CO_2$ reduction in $H_2O$/DMF (3:7 v/v) under reactions conditions that were otherwise the same, where CO was found to be the main product throughout the reaction (Figure 5). If the fact that $H_2O$ played the role of the proton source in the reduction of $CO_2$ affording CO and $HCOO^-$ is taken into account, the decrease in the formation rates of CO and $HCOO^-$ in $H_2O$/DMF (1:9 v/v) after 2 h (Figure 5), therefore, may be associated with the rapid decrease in the proton concentration in $H_2O$/DMF (1:9 v/v) compared with that in $H_2O$/DMF (3:7 v/v).

**Functions of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$.** Neither $[RuL_2(CO)_2]^{2+}$ (L = bpy, phen), TEOA, nor BNAH has any appreciable electronic absorption band above 400 nm in its electronic absorption spectra. Therefore, only $[Ru(bpy)_3]^{2+}$ is excited photochemically under irradiation with light ($\lambda > 400$ nm), suggesting that the excited-state $[Ru(bpy)_3]^{2+*}$ participates in the catalytic cycle of the present photochemical $CO_2$ reduction. As expected from the fact that $[Ru(bpy)_3]^{2+}$ has no catalytic ability in the $CO_2$ reduction, the direct electron transfer from $[Ru(bpy)_3]^{2+*}$ to $CO_2$ apparently is unreasonable on the basis of the oxidation potential of $[Ru(bpy)_3]^{2+*}$ (−0.81 V vs SCE).[46] Furthermore, the luminescence from $[Ru(bpy)_3]^{2+*}$ ($\lambda_{max} = 608$ nm) was not quenched at all by the presence of the experimental concentrations of $[Ru(bpy)_2(CO)_2]^{2+}$ (of the order 0.1 mmol dm$^{-3}$). Thus, the possibility of the electron transfer from the coordinatively saturated complex $[Ru(bpy)_3]^{2+*}$ to $CO_2$ or to $[Ru(bpy)_2(CO)_2]^{2+}$ is reasonably excluded in the present study. On the other hand, the luminescent state of $[Ru(bpy)_3]^{2+*}$ is reductively quenched by TEOA[23a] and BNAH[39] to produce $[Ru(bpy)_3]^+$ (eqs 3 and 4). The redox potential of the $[Ru(bpy)_3]^{+/2+}$ couple is −1.33 V vs SCE,[46] which is more negative than the reduction potential of $[Ru(bpy)_2(CO)_2]^{2+}$ (−0.98 V vs SCE)[3] and nearly the same potential as $[Ru(bpy)_2(CO)(COO^-)]^+$ (−1.30 V vs SCE), as discussed below. It is concluded, therefore, that $[Ru(bpy)_3]^+$ formed photochemically functions as a reductant of $[Ru(bpy)_2(CO)_2]^{2+}$.

$$[Ru(bpy)_3]^{2+*} + TEOA \rightarrow [Ru(bpy)_3]^+ + TEOA^{\bullet+} \quad (3)$$

$$[Ru(bpy)_3]^{2+*} + BNAH \rightarrow [Ru(bpy)_3]^+ + BNAH^{\bullet+} \quad (4)$$

**Mechanism of the Photochemical $CO_2$ Reduction Catalyzed by the $[Ru(bpy)_3]^{2+}/[Ru(bpy)_2(CO)_2]^{2+}$ System.** The preceding discussion reveals that (i) $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ function as photosensitizers and as catalysts in the photochemical $CO_2$ reduction, (ii) $HCOO^-$ is produced selectively in TEOA/DMF (1:4 v/v), (iii) the catalytic system is decomposed in dry DMF in the presence of BNAH, and (iv) not only $HCOO^-$ but also CO is formed in $H_2O$/DMF (1:9 v/v), where the mole ratio of CO to $HCOO^-$ decreased with the lapse of time. These results indicate that the protons released upon the dimerization of $BNAH^{\bullet+}$ (Experimental Section) formed in the reaction of eq 4 were not high enough in concentration to induce the catalytic reduction of $CO_2$ to $HCOO^-$ and CO and that the distribution of the actual catalysts for the formation of those products was controlled by the proton concentrations of the media used. Recently, we have demonstrated that the carbon atom of a carbonyl moiety of $[Ru(bpy)_2(CO)_2]^{2+}$ undergoes a reversible nucleophilic attack by $OH^-$ in $H_2O$ to afford $[Ru(bpy)_2(CO)(C(O)OH)]^+$ (eq 5), which dissociates the hydroxycarbonyl proton to generate a $CO_2$ adduct $[Ru(bpy)_2(CO)(COO^-)]^+$ in alkaline solutions (eq 6), and those three species exist as equilibrium mixtures in weak alkaline solutions.[32] In addition, the controlled-potential electrolysis of $[Ru(bpy)_2(CO)_2]^{2+}$ in $CO_2$-saturated dry DMF at −1.10 V vs SCE causes a dissociation of a CO ligand with generation of an unstable pentacoordinated complex $[Ru(bpy)_2(CO)]^0$ (18-electron species) (eq 7), which rapidly reacts with $CO_2$ to produce the $CO_2$ adduct also (eq 8). The reduced species of $[Ru(bpy)_2(CO)(COO^-)]^+$, however, is not so stable in the absence of a proton donor, since a prolonged electrolysis of $[Ru(bpy)_2(CO)(COO^-)]^+$ results in a gradual decomposition even in $CO_2$-saturated dry DMF.[3]

$$[Ru(bpy)_2(CO)_2]^{2+} + OH^- \rightleftharpoons [Ru(bpy)_2(CO)(C(O)OH)]^+ \quad (5)$$

$$[Ru(bpy)_2(CO)(C(O)OH)]^+ + OH^- \rightleftharpoons [Ru(bpy)_2(CO)(COO^-)]^+ + H_2O \quad (6)$$

$$[Ru(bpy)_2(CO)]^{2+} + 2e^- \rightarrow [Ru(bpy)_2(CO)]^0 + CO \quad (7)$$

$$[Ru(bpy)_2(CO)]^0 + CO_2 \rightarrow [Ru(bpy)_2(CO)(COO^-)]^+ \quad (8)$$

On the basis of above facts, the most plausible mechanism for the present photochemical reaction is as follows: the reduction of $[Ru(bpy)_2(CO)_2]^{2+}$ by two molecules of $[Ru(bpy)_3]^+$ generated photochemically (eqs 3 and 4) is followed by liberation of CO[3] with generation of $[Ru(bpy)_2(CO)(COO^-)]^+$ via $[Ru(bpy)_2(CO)]^0$ (eqs 7 and 8) in $CO_2$-saturated DMF. The interconversion between $[Ru(bpy)_2(CO)(COO^-)]^+$ and $[Ru(bpy)_2(CO(C(O)OH)]^+$ (eq 6) takes place in a diffusion-controlled reaction, and the latter is further converted to $[Ru(bpy)_2(CO)_2]^{2+}$ in neutral aqueous solutions.[32] The photochemical $CO_2$ reduction in $H_2O$/DMF (1:9 v/v), therefore, produces CO as the main product in the initial stages. The reduction of $CO_2$ to CO (eq 9) causes the basicity of the system to increase. Consequently, the equilibria described by eqs 5 and 6 are shifted toward the species $[Ru(bpy)_2(CO)(COO^-)]^+$, and the reduction of $[Ru(bpy)_2(CO)(C(O)OH)]^+$ or $[Ru(bpy)_2(CO)(COO^-)]^+$ by two molecules of $[Ru(bpy)_3]^+$, therefore, results in a predominant formation of $HCOO^-$ with regeneration of $[Ru(bpy)_2(CO)(COO^-)]^+$ via $[Ru(bpy)_2(CO)]^0$ under $CO_2$-saturated aqueous conditions. In order to confirm this assumption, the redox behavior of $[Ru(bpy)_2(CO)(COO^-)]^+$ prepared by the reaction of $[Ru(bpy)_2(CO)_2]^{2+}$ with $OH^-$ (eqs 5 and 6) was examined by means of cyclic voltammograms; $[Ru(bpy)_2(CO)_2]^{2+}$ undergoes an irreversible two-electron reduction at −0.98 V vs SCE in DMF (Figure 6a). The addition of 2 molar equiv of a methanolic solution of $Bu_4NOH$ to this solution results in the appearance of new redox couples due to $[Ru(bpy)_2(CO)(COO^-)]^+$[47] at $E_{1/2} = -1.30$ and −1.50 V ($E_{1/2} = (E^p_{red} + E^p_{ox})/-2$) at the expense of the −0.98-V cathodic wave

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (9)$$

---

(46) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

(47) This solution may involve $[Ru(bpy)_2(CO)(COOH)]^+$ in addition to $[Ru(bpy)_2(CO)(COO^-)]^+$. As the interconversion between these species takes place in a diffusion-controlled reaction, the redox reaction of each species cannot be distinguished by cyclic voltammograms.

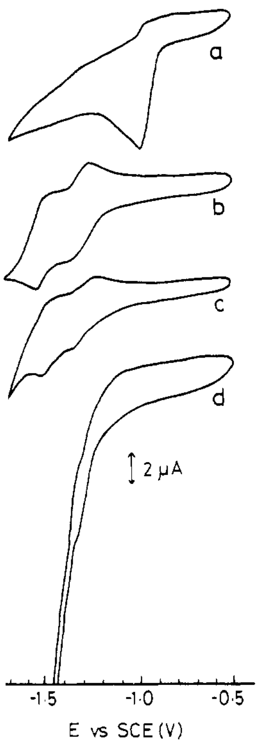


**Figure 6.** Cyclic voltammograms of $[Ru(bpy)_2(CO)_2(PF_6)_2$ (1.0 mmol $dm^{-3}$) in the absence (a) and presence (b) of a 2 molar equiv of $Bu_4NOH$ in DMF and those of the mixture of $[Ru(bpy)_2(CO)_2](PF_6)_2$ and a 2 molar excess of $Bu_4NOH$ in $N_2$-saturated TEOA/DMF (1:4 v/v) (c) and in $CO_2$-saturated TEOA/DMF (1:4 v/v) (d), with $dE/dt$ = 100 mV/s.

due to $[Ru(bpy)_2(CO)_2]^{2+}$ (Figure 6b). The peak potentials of the redox couples of $[Ru(bpy)_2(CO)(COO^-)]^+$ in DMF are essentially unchanged in TEOA/DMF (1:4 v/v) (Figure 6c). When $CO_2$ was bubbled into the TEOA/DMF (1:4 v/v) solution containing $[Ru(bpy)_2(CO)_2]^{2+}$ and a 2 molar equiv excess of $Bu_4NOH$, a strong irreversible cathodic current flowed at potentials more negative than −1.25 V and the threshold potential was consistent with that of the cathodic wave of the $E_{1/2} = -1.30$ V redox couple of $[Ru(bpy)_2(CO)(COO^-)]^+$. These results suggest that $[Ru(bpy)_2(CO)(COO^-)]^+$ also catalyzes the reduction of $CO_2$ at potentials more negative than −1.30 V in a $CO_2$-saturated TEOA/DMF solution. The selective formation of $HCOO^-$ in the photochemical $CO_2$ reduction in TEOA/DMF (1:4 v/v), therefore, mainly results from the reduction of $[Ru(bpy)_2(CO)(COO^-)]^+$ (or $[Ru(bpy)_2(CO)(C(O)OH)]^+$) by $[Ru(bpy)_3]^+$, where the hydroxy proton of TEOA or the β-proton of $TEOA^{\bullet +}$ ($pK_a = 7.8$)[46] functions as a proton source.

It has been reported that $Re(bpy)(CO)_3H$ reacts with $CO_2$ to afford $Re(bpy)(CO)_3OC(O)H$ quantitatively.[48] On the other hand, the hydrogen atom of $HCOO^-$ formed in the controlled-potential electrolysis of $[Os(bpy)_2(CO)H]^+$ in $CO_2$-saturated anhydrous $CH_3CN$ has been shown not to come from the hydride bonded to Os, and the same electrolysis conducted in the presence of $H_2O$ more than 0.3 mol $dm^{-3}$ in $CO_2$-saturated $CH_3CN$ results in a predominant $H_2$ evolution.[49] The present photochemical $CO_2$ reduction is accompanied by a trace amount of $H_2$ evolution; irradiation with visible light ($\lambda > 400$ nm) of $CO_2$-saturated $H_2O$/DMF (3:7 v/v) containing $[Ru(bpy)_3]^{2+}$ (0.5 mmol $dm^{-3}$), $[Ru(bpy)_2(CO)_2]^{2+}$ (0.1 mmol $dm^{-3}$), and BNAH (0.1 mol $dm^{-3}$) produced 63 μmol of CO, 23 μmol of $HCOO^-$, and less than 1 μmol of $H_2$ for 10 h (see Figure 5, where $H_2$ is omitted). When the same photochemical reaction was conducted in the absence of $CO_2$ in $H_2O$/DMF (3:7 v/v) under otherwise the same conditions, 47 μmol of $H_2$ was produced. The precursor to the $H_2$ formation may be a ruthenium–hydride species such as $[Ru(bpy)_2(CO)H]^+$, since that species is known to react with $H_2O$ to evolve $H_2$ in acidic conditions.[50] These results suggest that $[Ru(bpy)_2(CO)]^0$ formed in eq 7 in $H_2O$/DMF reacts with protons to generate $[Ru(bpy)_2(CO)H]^+$ (eq 10) in the absence of $CO_2$.

$$[Ru(bpy)_2(CO)]^0 + H^+ \rightarrow [Ru(bpy)_2(CO)H]^+ \qquad (10)$$

Accordingly, the reaction of eq 10 also may take place in $CO_2$-saturated $H_2O$/DMF, and the resulting $[Ru(bpy)_2(CO)H]^+$ may lead to generation of a formato complex as a precursor of $HCOO^-$ by the reaction with $CO_2$.[51] The alternation of the main product from CO to $HCOO^-$ with the lapse of time in the photochemical $CO_2$ reduction in $CO_2$-saturated $H_2O$/DMF (1:9 v/v) (Figure 4), however, indicates that $[Ru(bpy)_2(CO)(COO^-)]^+$ is a common intermediate in the formation of $HCOO^-$ and CO and that it is produced by the reaction of eq 8 under the present reaction conditions.

As discussed above, the acid–base equilibria of $[Ru(bpy)_2(CO)_2]^{2+}$ (eqs 5 and 6) depend on the concentrations of protons and control the selectivity for the formation of $HCOO^-$ and CO in the reduction of $CO_2$. The rate of the formation of $[Ru(bpy)_3]^+$ as a reductant of $[Ru(bpy)_2(CO)_2]^{2+}$, therefore, determines the efficiency of the catalytic system. The quantum yields for the formation of CO and $HCOO^-$ were 14.8 and 2.7%, respectively, in the presence of $[Ru(bpy)_3]^{2+}$ (0.50 mmol $dm^{-3}$), $[Ru(bpy)_2(CO)_2]^{2+}$ (0.10 mmol $dm^{-3}$), and BNAH (0.1 mol $dm^{-3}$) in $H_2O$/DMF (1:9 v/v). The value for CO is very close to that for the formation of $HCOO^-$ (14%) by the same catalytic system in the presence of TEOA (2.0 mol $dm^{-3}$) in DMF (Figures 2 and 3). On the other hand, the quantum yield for $HCOO^-$ drops to 2% (Figure 4) upon the same photochemical $CO_2$ reduction in the presence of 0.1 mol $dm^{-3}$ of TEOA in $CO_2$-saturated DMF. In addition, $H_2O$ lowers the electron-donating ability of TEOA due to the protonation equilibrium (eq 2), and the quantum yield for the formation of $HCOO^-$ was further decreased to 1% in $H_2O$/DMF (1:9 v/v) under reaction conditions that were otherwise the same. Such a distinct difference in the quantum yields of the photochemical $CO_2$ reduction using BNAH and TEOA may be associated with the quenching rate constants of $[Ru(bpy)_3]^{2+*}$ by BNAH, $k_q = 2.0 \times 10^8$ $mol^{-1}$ $dm^3$ $s^{-1}$, and by TEOA, $k_q = 1.7 \times 10^5$ $mol^{-1}$ $dm^3$ $s^{-1}$ (in DMF).[23a] This may be caused by a difference of the oxidation potentials of TEOA (+0.82 V vs SCE)[52] and BNAH (+0.57 V vs SCE).[39] Thus, BNAH is much superior to TEOA as a reductive quencher of $[Ru(bpy)_3]^{2+*}$.

With respect to the selective formation of $HCOO^-$ in the photochemical $CO_2$ reduction using a very high concentration of $[Ru(bpy)_3]^{2+}$ (11 mmol $dm^{-3}$) in TEOA/DMF (1:4 v/v), a formato complex arising from the reaction of $CO_2$ with bis(bipyridine)ruthenium hydride species formed by photolabilization of a bpy ligand of $[Ru(bpy)_3]^{2+}$ has been proposed as the precursor for the formation of $HCOO^-$.[20,53] In contrast to this, neither $HCOO^-$ nor CO was produced under irradiation with light ($\lambda > 400$ nm) of a $CO_2$-saturated $H_2O$/DMF (3:7 v/v) containing $[Ru(bpy)_3]^{2+}$ (11 mmol $dm^{-3}$) and BNAH (0.10 mol $dm^{-3}$) for 20 h, suggesting that such a bpy ligand dissociation from $[Ru(bpy)_3]^{2+}$ does not take place in $H_2O$/DMF (3:7 v/v). On the other hand, when the photochemical $CO_2$ reduction was conducted in the presence of $[Ru(bpy)_3]^{2+}$ (0.50 mmol $dm^{-3}$) and Ru-

---

(48) Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500.

(49) Bruce, M. R. M.; Megehee, E.; Sullivan, B. P.; Thorp, H.; O'Toole, T. R.; Downard, A.; Meyer, T. J. *Organometallics*, **1988**, *7*, 238.

(50) Kelly, J. M.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1986**, 1045.

(51) The catalytic systems composed of $[Ru(bpy)_3]^{2+}/[Ru(bpy)_2(CO)_2]$/BNAH and $[Ru(bpy)_3]^{2+}/[Ru(bpy)_2(CO)H]$/BNAH show the same reactivity in the present $CO_2$ reduction, since the photoirradiation ($\lambda > 400$ nm) of $CO_2$-saturated DMF/$H_2O$ (1:9 v/v) containing $[Ru(bpy)_3]^{2+}$ (0.5 mmol $dm^{-3}$), $[Ru(bpy)_2(CO)H]^{2+}$ (0.5 mmol $dm^{-3}$), and BNAH (0.1 mol $dm^{-3}$) essentially produced amounts of CO and $HCOO^-$ identical with those in Figure 4, and the amount of $H_2$ evolved was less than 1 μmol. Thus, the reduction of both $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)H]^+$ in $H_2O$/DMF affords $[Ru(bpy)_2(CO)_2]^0$ as a common intermediate for the $CO_2$ reduction and $H_2$ evolution.

(52) Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720.

(53) An irradiation with light ($\lambda > 400$ nm) of $CO_2$-saturated TEOA/DMF (1:4 v/v, 5 $cm^3$) containing a high concentration of $[Ru(bpy)_3]^{2+}$ (11 mmol $dm^{-3}$) selectively produced 997 μmol of $HCOO^-$ for 20 h under the present experimental conditions.

$(bpy)_2Cl_2$ (0.50 mmol dm$^{-3}$) under otherwise identical conditions, not only $HCOO^-$ (13.4 μmol) but also CO (47.2 μmol) was produced without accompanying $H_2$ evolution. Although the amounts of $HCOO^-$ and CO formed are small compared with those produced in the catalytic system composed of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ (Figure 5), the mole ratios of CO to $HCOO^-$ are essentially consistent for both systems. Thus, the selectivity for CO and $HCOO^-$ is mainly controlled by the medium rather than the difference between $Ru(bpy)_2Cl_2$ and $[Ru(bpy)_2(CO)_2]^{2+}$.

---

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

# Vanadium-Mediated Oxygen Atom Transfer Reactions

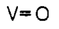
Yiping Zhang and R. H. Holm*

*Received June 19, 1989*

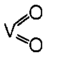
Oxygen atom (oxo) transfer reactions mediated at vanadium centers in oxidation states II–V have been demonstrated by using the set of complexes $VCl_2(py)_4$, $[VCl_4(MeCN)_2]^-$, $VOCl_2(py)_2$, $[VOCl_4]^{2-}$, $[VOCl_4]^-$, and $[VO_2Cl_2]^-$ and oxo donors/acceptors XO/X in acetonitrile solutions. This set should reflect the inherent reactivity of a given oxidation state in a somewhat conserved ligand environment, without undue ligand effects on reactivity. The following transformations have been proven, either by product isolation in good yield or by examination in situ by spectrophotometry or $^{51}V$ NMR spectroscopy: $V^{II} + XO \rightarrow V^{IV}O + X$; $V^{III} + XO \rightarrow V^{V}O + X$; $V^{V}O_2 + V^{III} \rightarrow 2V^{IV}O$; $V^{II} + V^{IV}O \rightarrow V^{III}\text{–O–}V^{III}$. The last process generates a compound (an intermediate in the first reaction) that has been isolated. $V_2OCl_4(py)_6\cdot MeCN$ crystallizes from acetonitrile/ether in monoclinic space group $C2/c$ with $a = 21.093\ (9)$ Å, $b = 33.885\ (9)$ Å, $c = 12.335\ (3)$ Å, $\beta = 124.33\ (2)°$, and $Z = 8$. There are two independent molecules with imposed 2-fold symmetry and essentially linear (178.7 (8)°) and exactly linear V–O–V bridges. Bridge distances are 1.77–1.78 Å, and each V(III) atom is in a distorted octahedral site. Other demonstrated transformations are the electron-transfer reaction $V^{II} + V^{V}O \rightarrow V^{III} + V^{IV}O$ and $V^{IV}O$ or $V^{V}O + XO \rightarrow V^{V}O_2 + X$ with evolution of chlorine when strong oxo donors (PhIO, $m\text{-}ClC_6H_4CO_3H$) are used. All oxo-transfer and related reactions that interconnect $V^{II,III}$ and the oxovanadium groups $V^{IV}O$, $V^{V}O$, $V^{V}{}_2O_3$, $V^{IV}V^{V}O_3$, and $V^{V}O_2$ are schematically summarized. This work provides the first systematic examination of the oxo-transfer reactions of V(II–V).

## Introduction

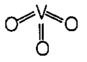
In our recent treatment of metal-centered oxygen (oxo) transfer reactions,[1] we have emphasized the functional group aspect of oxometal units, inasmuch as they frequently sustain regiospecific reaction chemistry. The most important oxovanadium groups are **1** and **2**, which have been structurally characterized in a variety of compounds.[1,2] Of such species, square-pyramidal $[VOX_4]^-$ ($X = Cl^-, Br^-$)[3,4] and $VO(acac)_2$[5] and distorted tetrahedral $[VO_2Cl_2]^-$[6] are among the simplest. Pyramidal group **3** is known only in insoluble metal salts of $[V_2O_7]^{4-}$,[7] and no reaction chemistry of it has been reported. Two remaining groups are derivatives of **2** by protonation or alkylation (**4**, R = H, alkyl) and of **1** and **2** by μ-oxo-bridge formation (**5**). Structurally characterized examples include $VO(O\text{-}i\text{-}Pr)(ox)_2$[8] and salts of the anion of $VO(OH)(ox)_2$[9,10] (**4**) and $V_2O_3(ox)_4$[11] and $[V_2O_3(peida)_2]^-$[12] (**5**). Bridge group **6** contains no terminal oxo ligands and is not a functional group in the sense of **1**, **2**, **4**, and **5**, but, as will be shown, it can be derived from an oxovanadium species. This bridge has been previously demonstrated in two compounds.[13,14]



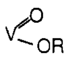
**1** ($d^{0,1}$)



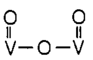
**2** ($d^0$)



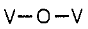
**3** ($d^0$)



**4** ($d^0$)



**5** ($d^{0/0,1}$)



**6** ($d^{2/2}$)

The functional group nature of oxovanadium is evident from the early work of Blair et al.,[15] who likened **4** (R = alkyl) to an organic ester and **5** to an anhydride. This concept has since been well developed in the form of a variety of substitution reactions at $V^{IV}{=}O$ groups[16–18] and by Floriani and co-workers,[10] who

**Table I.** Absorption Spectral Data for Vanadium(II–V) Complexes in Acetonitrile Solutions

| complex | $\lambda_{max}$, nm ($\epsilon_M$) |
|---|---|
| $VCl_2(py)_4$ | 255 (10 600), 411 (1790) |
| $[VCl_4(MeCN)_2]^-$ | 327 (3730) |
| $V_2OCl_4(py)_6$[a] | 252 (16 000), 290 (sh, 4200), 365 (1900), 538 (4100), 674 (sh, 1100) |
| $VOCl_2(py)_2$ | 340 (390), 788 (45) |
| $[VOCl_4]^{2-}$ | 424 (12), 734 (51) |
| $[VOCl_4]^-$ | 266 (6830), 487 (4770), 650 (180) |
| $[VO_2Cl_2]^-$ | 397 (265) |

[a] Extinction coefficients are approximate values.

---

(1) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.
(2) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988; pp 159–162.
(3) Beindorf, G.; Strähle, J.; Liebelt, W.; Dehnicke, K. *Z. Naturforsch.* **1980**, *35B*, 522.
(4) Müller, U.; Shihada, A.-F.; Dehnicke, K. *Z. Naturforsch.* **1982**, *37B*, 699.
(5) Dodge, R. P.; Templeton, D. H.; Zalkin, A. *J. Chem. Phys.* **1961**, *35*, 55. acac = acetylacetonate(1−).
(6) Fenske, D.; Shihada, A.-F.; Schwab, H.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1980**, *471*, 140.
(7) Au, P. K. L.; Calvo, C. *Can. J. Chem.* **1967**, *45*, 2297.
(8) Scheidt, W. R. *Inorg. Chem.* **1973**, *12*, 1758. ox = 8-hydroxyquinolinate(1−).
(9) Jeannin, Y.; Launay, J. P.; Sedjadi, M. A. S. *J. Coord. Chem.* **1981**, *11*, 27.
(10) Giacomelli, A.; Floriani, C.; Duarte, A. O.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1982**, *21*, 3310.
(11) Yamada, S.; Katayama, C.; Tanaka, J.; Tanaka, T. *Inorg. Chem.* **1984**, *23*, 253.
(12) Kojima, A.; Okazaki, K.; Ooi, S.; Saito, K. *Inorg. Chem.* **1983**, *22*, 1168. peida = ((1-(2-pyridyl)ethyl)imino)diacetate(2−).
(13) Chandrasekhar, P.; Bird, P. H. *Inorg. Chem.* **1984**, *23*, 3677.
(14) Money, J. K.; Folting, K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1987**, *26*, 944.
(15) Blair, A. J.; Pantony, D. A.; Minkoff, G. J. *J. Inorg. Nucl. Chem.* **1958**, *5*, 316.

0020-1669/90/1329-0911$02.50/0