CHEMISTRY LETTERS, pp. 339-342, 1988.

© 1988 The Chemical Society of Japan

Photochemical CO_2 . Reduction by an NADH Model Compound in the Presence of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ (bpy = 2,2'-bipyridine) in H_2O / DMF

Hitoshi ISHIDA, Koji TANAKA, and Toshio TANAKA^{*} Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

Photochemical conversion of CO_2 to CO and $HCOO^-$ was achieved by using an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), as an electron donor in the presence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) and $[Ru(bpy)_2(CO)_2]^{2+}$ in H_2O / DMF. The quantum yields for the CO and $HCOO^-$ formation attained 14.8 and 2.7%, respectively, in H_2O/DMF (1:9 v/v).

Electrochemical^{1,2)} and photochemical³⁻⁵⁾ CO_2 reduction catalyzed by metal complexes has been of much interest. The selective formation of CO and HCOO⁻ in the electrochemical CO_2 reduction has been achieved by adjusting the acidity of the proton sources.¹⁾ On the other hand, the photochemical CO_2 reduction reported so far has been conducted under strong basic conditions by using triethanolamine as an electron donor, where the formation of CO and HCOO⁻ seems to depend on the nature of catalysts; Ru^{3,4)} complexes selectively afford HCOO⁻, while an Re complex⁵⁾ gives only CO. Thus, photochemical CO_2 reduction under neutral protic conditions is desired in connection with the biochemical CO_2 fixation. Reduced nicotinamide adenine dinucleotide (NADH) functions as an electron donor in biological CO_2 fixation.⁶) There have been extensive studies on the chemistry of 1,4-dihydronicotinamides as a model for NADH, $^{7)}$ while no CO $_2$ reduction with an NADH model compound has been reported. This letter describes the first photochemical CO2 reduction by an NADH model compound, 1-benzyl-1,4dihydronicotinamide (BNAH), as an electron donor in H_2O/DMF containing $[Ru(bpy)_{2}(CO)_{2}]^{2+}$ and $[Ru(bpy)_{3}]^{2+}$.

Irradiation of visible light ($\lambda > 400 \text{ nm}$) to CO₂-saturated H₂O/DMF (3:7 and 1:9 v/v) solutions containing [Ru(bpy)₃]Cl₂·6H₂O (5.0 x 10⁻⁴ mol dm⁻³),

 $[Ru(bpy)_2(CO)_2](PF_6)_2$ (1.0 x 10⁻⁴ mol dm⁻³), and BNAH (0.10 mol dm⁻³) produces not only CO (Eq. 1) but also HCOO⁻ (Eq. 2).⁸) The result for the photochemical

$$CO_{2} + 2H^{+} + 2e^{-} \longrightarrow CO + H_{2}O \quad (1)$$

$$CO_{2} + H^{+} + 2e^{-} \longrightarrow HCOO^{-} \quad (2)$$

reaction conducted in H_2O/DMF with 3:7 v/v is illustrated in Fig. 1, which shows the amounts of products increasing with the lapse of time. The quantum yields for the CO and HCOO⁻ formation were $\phi_{CO} = 8.6$ % and $\phi_{HCOO^-} = 1.9$ % in H_2O/DMF with 3:7 v/v, and $\phi_{CO} = 14.8$ % and $\phi_{HCOO^-} = 2.7$ % in H_2O/DMF with 1:9 v/v.⁹⁾ On the other hand, neither CO nor HCOO⁻ was produced in a CO₂-saturated dry DMF under otherwise the same conditions,

suggesting that H_2O plays a role as a proton source in the present CO_2 reduction. In addition, the control experiments conducted in the absence of either one of $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(CO)_2]^{2+}$, and BNAH in H_2O/DMF (3:7 v/v) have also produced neither CO nor $HCOO^-$.

Thus, all the components are required to proceed the photochemical CO_2 reduction. The luminescence of $[Ru(bpy)_3]^{2+*}$ has, however, not been quenched at all by $[Ru(bpy)_2(CO)_2]^{2+}$ at the present experimental concentrations of the latter (the order of 10^{-4} mol dm⁻³) in DMF. On the other hand, BNAH $(E^0(BNAH/BNAH^{\ddagger}) = +0.57 \text{ V } \underline{vs}.$ SCE)¹⁰ reductively quenches the emitting exited state $[Ru(bpy)_3]^{2+*}$ with $k_q = 2.0 \times 10^8$



Fig. 1. Amounts of the products formed in the photochemical CO_2 reduction catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ (1.0 x 10^{-4} mol dm⁻³) in H_2O/DMF (3:7 v/v) containing $[Ru(bpy)_3]^{2+}$ (5.0 x 10^{-4} mol dm⁻³) and BNAH (0.10 mol dm⁻³); a 300 W-Hg lamp ($\lambda > 400$ nm). $mol^{-1} dm^3 s^{-1}$, affording $[Ru(bpy)_3]^+$ and BNAH[‡] (Eq. 3),¹¹) the latter of

$$[Ru(bpy)_3]^{2+*} + BNAH \longrightarrow [Ru(bpy)_3]^+ + BNAH^+ (3)$$

which is dimerized into $(BNA)_2$ with releasing protons.¹²⁾ On the other hand, $[Ru(bpy)_3]^+$ thus formed is a strong reducing agent with $E^0(Ru^+/Ru^{2+}) = -1.35 \text{ V} \underline{vs}$. $SCE,^{13)}$ which is very close to the potential (-1.30 V <u>vs.</u> SCE) applied for the CO_2 reduction by $[Ru(bpy)_2(CO)_2]^{2+}$ under the controlled potential electrolysis conditions.¹⁾ Thus, $[Ru(bpy)_2(CO)_2]^{2+}$ is stepwisely reduced by two moles of $[Ru(bpy)_3]^+$ as an electron mediator to give a coordinatively unsaturated Ru complex $[Ru(bpy)_2(CO)]^0$ with releasing a CO molecule (Eq. 4), the former of which reacts with CO_2 to give a formally Ru^{II} complex $[Ru(bpy)_2(CO)(COO^-)]^+$ (Eq. 5), as

$$[Ru(bpy)_{2}(CO)_{2}]^{2+} + 2[Ru(bpy)_{3}]^{+} \longrightarrow [Ru(bpy)_{2}(CO)]^{0} + CO + 2[Ru(bpy)_{3}]^{2+} (4)$$

$$[\operatorname{Ru}(\operatorname{bpy})_2(\operatorname{CO})]^0 + \operatorname{CO}_2 \longrightarrow [\operatorname{Ru}(\operatorname{bpy})_2(\operatorname{CO})(\operatorname{COO}^-)]^+$$
(5)

described in the electrochemical CO_2 reduction by $[Ru(bpy)_2(CO)_2]^{2+.1}$ The resulting $[Ru(bpy)_2(CO)(COO^-)]^+$ exists as an equilibrium mixture with $[Ru(bpy)_2(CO)C(0)OH]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$ (Eqs. 6 and 7), both of which are

$$[Ru(bpy)_2(CO)(COO^{-})]^+ + H^+$$
 [Ru(bpy)₂(CO)C(O)OH]^+ (6)

$$[Ru(bpy)_2(CO)C(O)OH]^+ + H^+ \longrightarrow [Ru(bpy)_2(CO)_2]^{2+} + H_2O$$
 (7)

further reduced by $[Ru(bpy)_3]^+$ to regenerate $[Ru(bpy)_2(CO)]^0$ with affording HCOO⁻ and CO, respectively.¹⁾ In view of the fact that the electrochemical CO₂ reduction by $[Ru(bpy)_2(CO)_2]^{2+}$ in acidic conditions (pH 6.0) yields CO selectively,¹⁾ the formation of CO as the main product in the present photochemical CO₂ reduction in H₂O/DMF may be interpreted in terms of acceleration of the conversion not only from $[Ru(bpy)_2(CO)(COO^-)]^+$ to $[Ru(bpy)_2(CO)C(O)OH]^+$ (Eq. 6) but also from $[Ru(bpy)_2(CO)C(O)OH]^+$ to $[Ru(bpy)_2(CO)_2]^{2+}$ (Eq. 7) by water. This is consistent with the fact that the similar photochemical CO₂ reduction conducted in the presence of a basic electron donor triethanolamine (0.10 mol dm⁻³) in DMF and in H₂O/DMF (1:9 v/v) containing $[Ru(bpy)_3]^{2+}$ (5.0 x 10⁻⁴ mol

341

 dm^{-3}) and $[Ru(bpy)_2(CO)_2]^{2+}$ (1.0 x 10^{-4} mol dm^{-3}) selectively affords HCOO⁻ with quantum yields 2 and 1%, respectively.¹⁴) Thus, BNAH is superior to triethanolamine as an electron donor in the photochemical CO₂ reduction.

This work was supported by General Sekiyu Research & Development Encouragement & Assistance Foundation.

- References
- H. Ishida, K. Tanaka, and T. Tanaka, Organometallics, <u>6</u>, 181 (1987); H. Ishida, H. Tanaka, K. Tanaka, and T. Tanaka, J. Chem. Soc., Chem. Commun., <u>1987</u>, 131.
- 2) M. Beley, J.-P. Collin, R. Ruppert, and J.-P. Sauvage, J. Am. Chem. Soc., <u>108</u>, 7461 (1986); M. Nakazawa, Y. Mizobe, Y. Matsumoto, Y. Uchida, M. Tezuka, and M. Hidai, Bull. Chem. Soc. Jpn., <u>59</u>, 809 (1986); D. L. DuBois and A. Miedarner, J. Am. Chem. Soc., <u>109</u>, 113 (1987); J. Hawecker, J.-M. Lehn, and R. Ziessel, J. Chem. Soc., Chem. Commun., <u>1984</u>, 328; S. Slater and J. H. Wagenknecht, J. Am. Chem. Soc., <u>106</u>, 5367 (1984).
- 3) H. Ishida, K. Tanaka, and T. Tanaka, Chem. Lett., 1987, 1035.
- J. Hawecker, J.-M. Lehn, and R. Ziessel, J. Chem. Soc., Chem. Commun., <u>1985</u>, 56; N. Kitamura and S. Tazuke, Chem. Lett., <u>1983</u>, 1109.
- 5) J. Hawecker, J.-M. Lehn, and R. Ziessel, J. Chem. Soc., Chem. Commun., <u>1983</u>, 536.
- D. I. Arnon, "Bioorganic Chemistry IV," ed by E. E. van Tamelen, Academic Press, New York (1978), p. 4.
- S. Fukuzumi, K. Hironaka, and T. Tanaka, J. Am. Chem. Soc., <u>105</u>, 4722 (1983), and references therein.
- 8) Photochemical CO_2 reductions were conducted in a septum capped Pyrex tube under irradiation of visible light ($\lambda > 400$ nm; a 300 W-Hg lamp equipped with an NaNO₂ chemical filter). CO and HCOO⁻ were determined by a gaschromatograph and an isotachophoretic analyser, respectively.
- 9) The quantum yield was determined by an Ushio model UI-501 xenon lamp through a Toshiba glass filter Y-43 (λ > 400 nm). Potassium ferrioxalate was used as an actinometer.
- S. Fukuzumi, S. Koumitsu, K. Hironaka, and T. Tanaka, J. Am. Chem. Soc., <u>109</u>, 305 (1987).
- 11) The k_q value was determined in DMF; C. Pac, Y. Miyauchi, O. Ishitani, M. Ihama, M. Yasuda, and H. Sakurai, J. Org. Chem., <u>49</u>, 26 (1984).
- 12) The formation of 4,4'- and 4,6'-linked BNA dimers were confirmed by comparison with the authentic samples in the liquid chromatography; Y. Ohnishi and M. Kitami, Bull. Chem. Soc. Jpn., <u>52</u>, 2674 (1979).
- 13) R. Ballardini, G. Varani, M. T. Indelli, F. Scandola, and V. Balzani, J. Am. Chem. Soc., <u>100</u>, 7219 (1978).
- 14) The decrease in the amount of $HCOO^{-}$ formed in H_2O/DMF (1:9 v/v) compared with that in DMF may be caused by the protonation to triethanolamine (pKa = 7.9) in the former.

(Received November 6, 1987)