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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

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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 photochemical[3-5] 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 complex[5] 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 CO_2 reduction by an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (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 ($\lambda > 400$ nm) to CO_2-saturated H_2O/DMF (3:7 and 1:9 v/v) solutions containing $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (5.0×10^{-4} mol dm^{-3}),

$[Ru(bpy)_2(CO)_2](PF_6)_2$ (1.0×10^{-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

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O \quad (1)$$

$$CO_2 + H^+ + 2e^- \longrightarrow HCOO^- \quad (2)$$

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 Φ_{CO} = 8.6% and Φ_{HCOO^-} = 1.9% in H_2O/DMF with 3:7 v/v, and Φ_{CO} = 14.8% and Φ_{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 CO_2-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$^+$) = +0.57 V vs. SCE)[10] reductively quenches the emitting exited state $[Ru(bpy)_3]^{2+*}$ with $k_q = 2.0 \times 10^8$

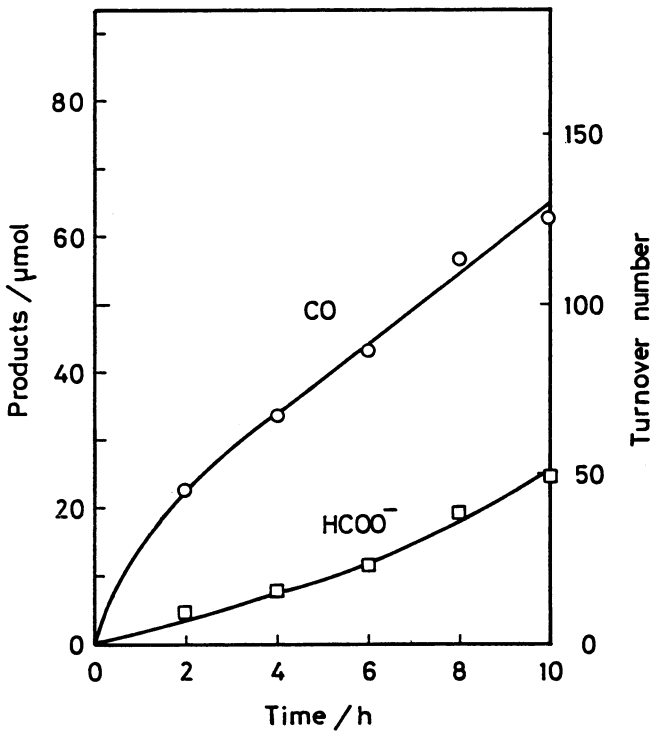

Fig. 1. Amounts of the products formed in the photochemical CO_2 reduction catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ (1.0×10^{-4} mol dm^{-3}) in H_2O/DMF (3:7 v/v) containing $[Ru(bpy)_3]^{2+}$ (5.0×10^{-4} mol dm^{-3}) and BNAH (0.10 mol dm^{-3}); a 300 W-Hg lamp ($\lambda > 400$ nm).

mol^{-1} dm^3 s^{-1}, affording $[Ru(bpy)_3]^+$ and $BNAH^{\ddagger}$ (Eq. 3),[11] the latter of

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

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 V vs. SCE,[13] which is very close to the potential (-1.30 V vs. 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

$$[Ru(bpy)_2(CO)_2]^{2+} + 2[Ru(bpy)_3]^+ \longrightarrow [Ru(bpy)_2(CO)]^0 + CO + 2[Ru(bpy)_3]^{2+} \quad (4)$$

$$[Ru(bpy)_2(CO)]^0 + CO_2 \longrightarrow [Ru(bpy)_2(CO)(COO^-)]^+ \quad (5)$$

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 $[Ru(bpy)_2(CO)C(O)OH]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$ (Eqs. 6 and 7), both of which are

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

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

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 CO_2 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 CO_2 reduction in H_2O/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 CO_2 reduction conducted in the presence of a basic electron donor triethanolamine (0.10 mol dm^{-3}) in DMF and in H_2O/DMF (1:9 v/v) containing $[Ru(bpy)_3]^{2+}$ (5.0×10^{-4} mol

dm^{-3}) and $[Ru(bpy)_2(CO)_2]^{2+}$ (1.0×10^{-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 CO_2 reduction.

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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 $NaNO_2$ 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 ($\lambda > 400$ nm). Potassium ferrioxalate was used as an actinometer.
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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.

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