

Photoreduction of CO₂ in the [Ru(bpy)₂(CO)₂]²⁺ / [Ru(bpy)₃]²⁺ or [Ru(phen)₃]²⁺
/ Triethanolamine / N,N-Dimethylformamide System

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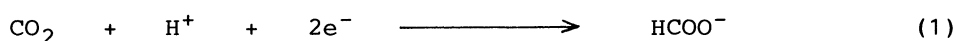
The [Ru(bpy)₂(CO)₂]²⁺ / [Ru(bpy)₃]²⁺ (or [Ru(phen)₃]²⁺) / triethanolamine / N,N-dimethylformamide system reduces CO₂ to afford HCOO⁻ efficiently under the irradiation of light ($\lambda > 320$ nm), where each of the former three components functions as a catalyst, a photosensitizer, and an electron donor, respectively.

The reduction of CO₂ by using transition metal complexes as photosensitizers (or photocatalysts) have recently been reported.¹⁻⁵⁾ There is, however, some confusion on the function of [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) in the photoreduction of CO₂ to give HCOO⁻; [Ru(bpy)₃]²⁺ was first reported to reduce CO₂ to HCOO⁻ in the presence of methylviologen (MV²⁺) in a mixture triethanolamine (TEOA) / N,N-dimethylformamide (DMF) under the irradiation of light ($\lambda > 320$ nm).¹⁾ Even in the absence of MV²⁺, however, the photoreduction of CO₂ was successfully proceeded by the irradiation of visible light ($\lambda > 400$ nm) in the presence of [Ru(bpy)₃]²⁺ with a high concentration (1.1×10^{-2} mol dm⁻³) in the same solvent system, where [Ru(bpy)₂(CO)X]⁺ (X = H, Cl) generated by the dissociation of bpy has been suggested to function as a photocatalyst to produce HCOO⁻ efficiently.²⁾ Moreover, the formation of HCOO⁻ in the [Ru(bpy)₃]²⁺ / MV²⁺ / TEOA / DMF system has been suggested to come from the decomposition of TEOA used as an electron donor.³⁾ We have recently reported that [Ru(bpy)₂(CO)₂]²⁺ is an efficient catalyst in the electrochemical CO₂ reduction.^{6,7)} This communication reports that [Ru(bpy)₂(CO)₂]²⁺ may be an efficient catalyst also for the photoreduction of CO₂ in the [Ru(bpy)₂(CO)₂]²⁺ / [Ru(bpy)₃]²⁺ or [Ru(phen)₃]²⁺

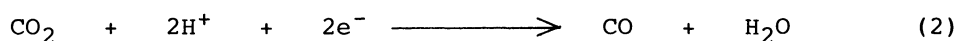
(phen = 1,10-phenanthroline) / TEOA / DMF system, where $[\text{Ru}(\text{bpy})_3]^{2+}$ or $[\text{Ru}(\text{phen})_3]^{2+}$ functions only as a photosensitizer.

Photoreduction of CO_2 was conducted in a septum-capped pyrex tube by irradiating light ($\lambda > 320 \text{ nm}$; a 300 W-Hg lamp equipped with a CuSO_4 chemical filter) for 20 h to a CO_2 -saturated TEOA/DMF (1:4 v/v, 5 cm^3) solution containing a given amount of either $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ or $[\text{Ru}(\text{bpy})_2(\text{CO})_2](\text{PF}_6)_2$, or both of them. The reaction products in the liquid and gaseous phases were analyzed by a Shimadzu IP-2A isotachophoretic analyzer and a Shimadzu GC-3BT gaschromatograph, respectively.

The photoreduction of CO_2 in a CO_2 -saturated TEOA/DMF in the presence of a low concentration ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) of $[\text{Ru}(\text{bpy})_3]^{2+}$ yields a small amount of HCOO^- (Eq. 1, entry 1 in Table 1). The addition of $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ to the



solution of $[\text{Ru}(\text{bpy})_3]^{2+}$, however, results in a drastic increase of HCOO^- (entries 2 - 5), with the concomitant production of trace amounts of CO and H_2 (Eqs. 2 and 3). On the other hand, no photoreduction of CO_2 occurs in the presence of only



$[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ (entry 6), which exhibits no electronic absorption band in the visible region.⁸⁾ Thus, $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ (λ_{max} : 452 nm) may function as an efficient catalyst and a photosensitizer, respectively, in the photoreduction of CO_2 . This assumption is consistent with the facts that (i) the amount of HCOO^- formed in the reduction of CO_2 for a given time increases with increasing the amount of $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ in the presence of a given concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ (entries 2 - 5), while the turnover number for the formation of HCOO^- based on $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ increases with decreasing the concentration of $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ to attain 3580 with its low concentration (entry 2), and (ii) the photoreduction of CO_2 similarly proceeded in CO_2 -saturated TEOA/DMF (1:4 v/v) containing both $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ (5.0×10^{-4}

Table 1. Reduction of CO₂ in the [Ru(bpy)₂(CO)₂]²⁺ / [Ru(bpy)₃]²⁺ / TEOA / DMF system by irradiation of the light λ > 320 nm for 20 h

Entry	Concentration / mol dm ⁻³		HCOO ⁻ / μmol	Turnover number ^{a)} based on [Ru(bpy) ₂ (CO) ₂] ²⁺
	[Ru(bpy) ₂ (CO) ₂] ²⁺	[Ru(bpy) ₃] ²⁺		
1	0	5.0 × 10 ⁻⁴	7	—
2	1.0 × 10 ⁻⁵	5.0 × 10 ⁻⁴	186	3580
3	5.0 × 10 ⁻⁵	5.0 × 10 ⁻⁴	258	1004
4	1.0 × 10 ⁻⁴	5.0 × 10 ⁻⁴	315	616
5	5.0 × 10 ⁻⁴	5.0 × 10 ⁻⁴	394	155
6	5.0 × 10 ⁻⁴	0	0	0

a)
$$\frac{\{\mu\text{mol of HCOO}^- \text{ produced in the presence of } [\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+} - 7 \mu\text{mol}\}}{\{\mu\text{mol of } [\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}\}}$$

mol dm⁻³) and [Ru(phen)₃]²⁺ (5.0 × 10⁻⁴ mol dm⁻³) to yield HCOO⁻ (139 μmol for 20 h); the latter Ru complex has been reported to exhibit no catalytic activity in the photoreduction of CO₂.²⁾

The ¹³C-NMR spectrum of the reaction mixture obtained after the photoreduction of ¹³CO₂ for 20 h in the medium TEOA/DMF/DMF-d⁷ (2:3:5 v/v) containing equal amounts of [Ru(bpy)₂(CO)₂]²⁺ and [Ru(bpy)₃]²⁺ (5.0 × 10⁻⁴ mol dm⁻³), showed an H¹³COO⁻ signal at δ 168.1, and the amount determined from the signal intensity of the ¹³C-NMR spectrum was consistent with that determined by the isotachophoretic analysis, suggesting that the formation of HCOO⁻ does not arise from the decomposition of TEOA.

The photoreduction of CO₂ may be initiated by the formation of a luminescent state [Ru(bpy)₃]^{2+*}, which is reductively quenched by TEOA to produce [Ru(bpy)₃]⁺ and the TEOA^{•+} radical cation.⁹⁾ The redox potential of the [Ru(bpy)₃]^{2+ / +} couple is -1.35 V vs. SCE,¹⁰⁾ which is not only more negative than the potential required for the two-electron reduction of [Ru(bpy)₂(CO)₂]²⁺ (-0.95 V vs. SCE in CH₃CN) but also very close to the potential (-1.30 V vs. SCE) applied for the successful electrochemical CO₂ reduction catalyzed by [Ru(bpy)₂(CO)₂]²⁺ in H₂O/DMF and MeOH⁷⁾. This suggests that the mechanism of the present photochemical CO₂ reduction is essentially the same as that of the electrochemical CO₂ reduction

reported previously,⁶⁾ and the proton source in the former may be either a hydroxyl proton of TEOA or a β -hydrogen ($pK_a = 7.8$)¹¹⁾ of TEOA[†].

It should finally be mentioned that $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$ as a possible impurity involved in $[\text{Ru}(\text{bpy})_3]^{2+}$ may cause a puzzling situation in understanding the mechanism of CO_2 reductions with $[\text{Ru}(\text{bpy})_3]^{2+}$ as a photosensitizer since not only the impurity is almost inevitable in $[\text{Ru}(\text{bpy})_3]^{2+}$ prepared from $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and 2,2'-bipyridine by refluxing in MeOH or DMF¹²⁾ but also it is an efficient catalyst in the electrochemical CO_2 reduction.⁶⁾ Such any catalytically active species as $[\text{Ru}(\text{bpy})_2(\text{CO})\text{X}]^+$ ($\text{X} = \text{H}, \text{Cl}$) may be photochemically generated from $[\text{Ru}(\text{bpy})_3]^{2+}$ in TEOA/DMF.²⁾

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- 9) The quenching rate constant was reported as $1.7 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$,⁴⁾ and $[\text{Ru}(\text{bpy})_3]^{2+*}$ was not quenched by $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ in DMF. Decomposition products of TEOA[†] were identified as diethanolamine and hydroxyacetaldehyde.²⁾
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