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Photoreduction of CO_2 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 CO_2 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 CO_2 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 CO_2 to give $HCOO^-$; $[Ru(bpy)_3]^{2+}$ was first reported to reduce CO_2 to $HCOO^-$ in the presence of methylviologen (MV^{2+}) in a mixture triethanolamine (TEOA) / N,N-dimethylformamide (DMF) under the irradiation of light ($\lambda > 320$ nm).[1] Even in the absence of MV^{2+}, however, the photoreduction of CO_2 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 $[Ru(bpy)_3]^{2+}$ / MV^{2+} / 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 CO_2 reduction.[6,7] This communication reports that $[Ru(bpy)_2(CO)_2]^{2+}$ may be an efficient catalyst also for the photoreduction of CO_2 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 $[Ru(bpy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$ functions only as a photosensitizer.

Photoreduction of CO_2 was conducted in a septum-capped pyrex tube by irradiating light (λ > 320 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 $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ or $[Ru(bpy)_2(CO)_2](PF_6)_2$, 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 (5.0×10^{-4} mol dm^{-3}) of $[Ru(bpy)_3]^{2+}$ yields a small amount of $HCOO^-$ (Eq. 1, entry 1 in Table 1). The addition of $[Ru(bpy)_2(CO)_2]^{2+}$ to the

$$CO_2 + H^+ + 2e^- \longrightarrow HCOO^- \qquad (1)$$

solution of $[Ru(bpy)_3]^{2+}$, 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

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

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (3)$$

$[Ru(bpy)_2(CO)_2]^{2+}$ (entry 6), which exhibits no electronic absorption band in the visible region.[8] Thus, $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ (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 $[Ru(bpy)_2(CO)_2]^{2+}$ in the presence of a given concentration of $[Ru(bpy)_3]^{2+}$ (entries 2 - 5), while the turnover number for the formation of $HCOO^-$ based on $[Ru(bpy)_2(CO)_2]^{2+}$ increases with decreasing the concentration of $[Ru(bpy)_2(CO)_2]^{2+}$ 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 $[Ru(bpy)_2(CO)_2]^{2+}$ (5.0×10^{-4}

Table 1. Reduction of CO_2 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) $$\frac{\{\mu\text{mol of } HCOO^- \text{ produced in the presence of } [Ru(bpy)_2(CO)_2]^{2+} - 7\ \mu\text{mol}\}}{\{\mu\text{mol of } [Ru(bpy)_2(CO)_2]^{2+}\}}$$

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 CO_2.[2)]

The ^{13}C-NMR spectrum of the reaction mixture obtained after the photoreduction of $^{13}CO_2$ for 20 h in the medium TEOA/DMF/DMF-d^7 (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 $H^{13}COO^-$ signal at δ 168.1, and the amount determined from the signal intensity of the ^{13}C-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 CO_2 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 $TEOA^{\dot{+}}$ radical cation.[9)] The redox potential of the $[Ru(bpy)_3]^{2+/+}$ couple is -1.35 V <u>vs</u>. 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 <u>vs</u>. SCE in CH_3CN) but also very close to the potential (-1.30 V <u>vs</u>. SCE) applied for the successful electrochemical CO_2 reduction catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ in H_2O/DMF and MeOH[7)]. This suggests that the mechanism of the present photochemical CO_2 reduction is essentially the same as that of the electrochemical CO_2 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 $TEOA^{\ddagger}$.

It should finally be mentioned that $[Ru(bpy)_2(CO)Cl]^+$ as a possible impurity involved in $[Ru(bpy)_3]^{2+}$ may cause a puzzulling situation in understanding the mechanism of CO_2 reductions with $[Ru(bpy)_3]^{2+}$ as a photosensitizer since not only the impurity is almost inevitable in $[Ru(bpy)_3]^{2+}$ prepared from $RuCl_3 \cdot nH_2O$ and 2,2'-bipyridine by refluxing in MeOH or DMF$^{12)}$ but also it is an efficient catalyst in the electrochemical CO_2 reduction.$^{6)}$ Such any catalytically active species as $[Ru(bpy)_2(CO)X]^+$ (X = H, Cl) may be photochemically generated from $[Ru(bpy)_3]^{2+}$ in TEOA/DMF.$^{2)}$

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