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Enhanced *p*-Terphenyl-Catalyzed Photoreduction of CO_2 to CO through the Mediation of Co(III)-Cyclam Complex

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Efficient *p*-terphenyl-catalyzed photoreduction of CO_2 to carbon monoxide can be achieved by combination with Cobalt^{3+}-cyclam (cyclam = 1,4,8,11-tetra-azacyclotetradecane) as an electron mediator in organic solvent.

Carbon dioxide fixation has been a subject of active interest in view of the global greenhouse effect. In particular, electrochemical and photochemical reductions of CO_2 have been extensively studied.1) Recently, we reported that *p*-terphenyl induces photoreduction of CO_2 to formic acid (HCO_2^-) and a small quantity of CO under >290-nm irradiation in N,N-dimethylformamide (DMF) containing triethylamine (TEA) as a sacrificial electron donor.2) Taking into account the role of cyclam metal complexes as mediators for electroreduction of CO_2,3,4) we investigated *p*-terphenyl-catalyzed CO_2 photoreduction in the presence of metal cyclam complexes as electron mediators in order to evaluate their abilities of electron mediation in this system.

As cyclam metal complexes, [Co(III)-cyclamCl_2]Cl (Co^{3+}-cyclam) and [Ni(II)-cyclam]Cl_2 (Ni^{2+}-cyclam) were prepared according to literatures.5) When a CO_2-saturated solution [2 cm^3 AN, 0.5 cm^3 methanol, and 0.5 cm^3 TEA] containing *p*-terphenyl (2×10^{-3} mol dm^{-3}), $[Co(cyclam)Cl_2]^+$ (1.7×10^{-3} mol dm^{-3}) was irradiated in a Pyrex tube (8 mm in diameter, 200 mm in length) with a 500 W high pressure Hg lamp, CO was formed with a less quantity of HCO_2^- and H_2 (Table 1, run 1). Methanol was added to dissolve cyclam metal complexes in the reaction system. When DMF/methanol was used instead of AN/methanol, the formation of HCO_2^- was suppressed and only CO was found as a reduction product from CO_2 (run 2). Mass spectroscopy and ^{13}C-NMR confirmed the formation of ^{13}CO (m/z = 29) and $H^{13}CO_2^-$ (δ = 169.3 ppm) in the photoreduction of $^{13}CO_2$. In the absence of any one of CO_2, light, TEA and *p*-terphenyl, neither CO nor HCO_2^- were formed. We reported in our previous paper that *p*-terphenyl-catalyzed photoreduction of CO_2 in DMF leads to the effective formation of HCO_2^- with a small quantity of CO, while the activity in AN is inferior to that in DMF.2) However, the presence of methanol in both cases suppressed the photoreduction of CO_2 (run 3, 4). These observations indicate that the introduction of Co^{3+}-cyclam leads to efficient photoreduction of CO_2 even in AN/methanol system. It is also worth noting that the selectivity for the formation of CO in both AN/ and DMF/methanol systems was enhanced. On the other hand, contrary to our expectation, neither $CoCl_2$ (run 5) nor Ni^{2+}-cyclam (run 6) functioned as electron mediators for the present reduction of CO_2. The latter result is in quite conflict with its role of electron mediator in the electroreduction of CO_2.3,4)

It was reported that tetraazamacrocyclic complexes of cobalt and nickel work as electron mediators in

Table 1. Photochemical System for Generation of CO, HCO_2^-,and H_2 from *p*-Terphenyl, $[Co(cyclam)Cl_2]Cl$, TEA, and CO_2 in CH_3CN/Methanolb)

Run	Solvent	Co^{3+}-cyclam	CO/ µmol	HCO_2^-/ µmol	H_2/ µmol	Product Ratio	
						CO/HCO_2^-	$(CO+HCO_2^-)/H_2$
1	AN/MeOH	a)	24	12	3.7	2.0	9.7
2	DMF/MeOH	a)	27	0	4.1	-	6.6
3	AN/MeOH	0	0	0	0.02	-	0
4	DMF/MeOH	0	0.20	0	0.09	-	-
5	AN/MeOH	$CoCl_2$	0	0	2.4	-	0
6	AN/MeOH	Ni^{2+}-cyclam	0	0	0.17	-	0
7	AN/H_2O	a)	2.8	7.5	1.5	0.37	6.9
8c)	AN/MeOH	a)	52	34	3.4	1.5	25

a) Present in reaction solution prior to photolysis; 0, absent from reaction solution prior to photolysis.
b) After irradiation at > 290 nm for 1 h. c) With TEOA instead of TEA.

the Ru(2,2'-bipyridine)$_3^{2+}$-catalyzed photoreduction of CO_2.6,7) These systems resulted in the formation of CO with H_2, suggesting the low selectivity for the reduction of CO_2 in water. However, the present system gave the enhanced selectivity shown by $(CO + HCO_2^-)/H_2$ ratios, 7 to 10. In order to confirm the selectivity under H^+-rich conditions, the photoreaction was conducted in the presence of H_2O (run 7). Although the efficiency decreased to fair extent and the formation of HCO_2^- increased, the photoreduction of CO_2 occur in preference to H^+ or water reduction in the system. Interestingly, when triethanolamine (TEOA) was used instead of TEA as an electron donor, the highest yield and selectivity for photoreduction of CO_2 were obtained (run 8), probably due to the higher solubility of CO_2. The apparent quantum yields, 0.15 and 0.10, were obtained for the formation of CO and HCO_2^- in TEOA system at 313 nm, respectively. In conclusion, we have shown that Co^{3+}-cyclam is a highly efficient and selective electron mediator for *p*-terphenyl-catalyzed photoreduction of CO_2 to CO. Further mechanistic studies on this CO_2-photoreduction system are in progress.

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