CHEMISTRY LETTERS, pp. 2047-2048, 1990.

Photochemical Reduction of Carbon Dioxide to Formate Catalyzed by *p*-Terphenyl in Aprotic Polar Solvent

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Photoreduction of CO_2 to formic acid and a small quantity of CO can be achieved in aprotic polar solvent by using *p*-terphenyl as catalyst and triethylamine as a sacrificial electron donor under >290-nm irradiation.

Carbon dioxide fixation using light energy has attracted much interest in view of the grobal greenhouse effect. Electrochemical and photochemical reduction of CO_2 were extensively studied and novel photocatalysts or photosensitizers have been requisite for the purpose.$^{1-4)}$ Recently, we reported that *p*-terphenyl effectively catalyzes the photoreduction of acetaldehyde to ethanol with triethylamine (TEA) as a sacrificial electron donor under UV-light irradiation.$^{5)}$ Here, we report that *p*-terphenyl induces effective photoreduction of CO_2 to formate and carbon monoxide (CO) in aprotic polar solvent.

In a Pyrex tube (8 mm in diameter) were placed distilled TEA (0.5 cm^3), anhydrous organic solvent (1.0 cm^3) and 10 mg of *p*-terphenyl (nacalai tesque) or poly(*p*-phenylene) (PPP) (synthesized by Yamamoto's method). After purging with CO_2 gas, the tube was closed off with a gum stopper, and irradiated under magnetic stirring for 15 h at >290 nm with a 500 W high-pressure mercury arc lamp. The products were analyzed by GLPC using an activated carbon column and by HPLC using a Tosoh anion-exclusion column with aqueous phosphate as eluent (2×10^{-3} mol dm^{-3}).

As is shown in Table 1, the photoreductive formation of formate and CO in anhydrous organic solvent systems was observed, where the photocatalysis of *p*-terphenyl in N,N-dimethylformamide (DMF) led to the most effective formation of formate and CO (the quantum yield ($\Phi_{1/2HCOOH}$) was 0.072 at 313 nm.). A trace amount of H_2 was detectable. As organic solvent, methanol and ethanol were not suitable for this reaction, but in tetrahydrofuran (THF) and acetonitrile (CH_3CN), small amounts of formate and CO were detected. The turnover number of *p*-terphenyl for the formation of $HCOO^-$ in DMF is about 3, implying a cyclic activity of the system. No formate was observed when the experiments were conducted in the absence of any one of light, CO_2, photocatalysts, and TEA. These results imply that all of the components are essential for the photoreduction of CO_2. Furthermore, the conversion of $^{13}CO_2$ into $H^{13}COO^-$ was clearly indicated by ^{13}C-NMR spectroscopy, which showed the increase of the $H^{13}COO^-$ resonance at δ=166.2 ppm under irradiation. The rate in the increase of the signal intensity was almost consistent with the rate determined by HPLC analysis.

Table 1. Photochemical Reduction of CO_2 Catalyzed by Terphenyls in Anhydrous Organic Solvent

Catalyst	Solvent	Photoproduct/ μmol[a]			Solubility in solvent	
	1.0 cm^3	$HCOO^-$	CO	H_2	Catalyst[b] mg/cm^3	CO_2[c] $X_2 \times 10^4$
p-terphenyl	DMF	42	5.6	1.1	6.6	202
o-terphenyl	DMF	1.9	0.1	0.4	670	202
m-terphenyl	DMF	3.6	0.3	0.7	207	202
PPP	DMF	3.8	1.0	2.9	0	202
None	DMF	0	0.2	0.1	-	202
p-terphenyl	CH_3CN	11	0.2	0.4	0.83	195
o-terphenyl	CH_3CN	0.3	0	0.2	500	195
m-terphenyl	CH_3CN	1.0	0.1	0.1	42	195
PPP	CH_3CN	1.0	0.3	7.7	0	195
None	CH_3CN	0	0	0.1	-	195
p-terphenyl	CH_3OH	0	0	0.2	0.28	56
p-terphenyl	C_2H_5OH	0	0.8	0.3	-	64
p-terphenyl	THF	4.8	1.2	0.2	>1.0	100

a) After irradiation at >290 nm for 15 h. b) Solubility of terphenyls in each solvent at room temperature. c) Mole fraction of the dissolved CO_2 gas in each solvent at 25 ℃.[6)]

It is interesting to note that CO_2 is well soluble in DMF and the solubility of *p*-terphenyl is relatively higher in DMF than in other organic solvents. However, *o*-terphenyl or *m*-terphenyl which are both very soluble in aprotic polar solvent showed much poorer activity than *p*-terphenyl, suggesting that *p*-phenylene unit is an important factor for the effective charge separation and electron transfer. In addition, insoluble PPP catalyzed the photoreduction of CO_2 to formate and CO in DMF and CH_3CN with low efficiency. It was previously reported[2)] that photocarboxylation of aromatic hydrocarbons such as phenanthrene, anthracene, and biphenyl occurs in photolyses in the presence of various amines and CO_2 of their dimethyl sulfoxide and DMF solution. In the present photolysis, however, no photocarboxylation was observed. In conclusion, the results in Table 1 indicate the first example of direct photoreduction of CO_2 catalyzed by organic sensitizer without an electron mediator.[3)] Futher studies on the novel photochemical reduction of CO_2 are in progress.

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(Received August 2, 1990)