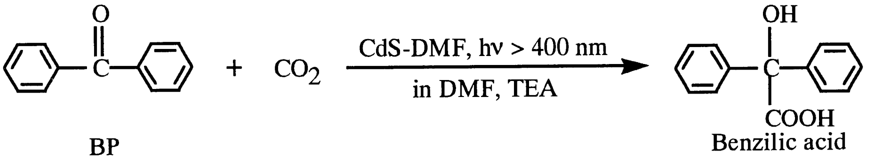
CHEMISTRY LETTERS, pp. 2113-2114, 1992.

Visible-Light Induced Photofixation of CO_2 into Benzophenone Catalyzed by Colloidal CdS Microcrystallites1)

Masashi KANEMOTO, Hirofumi ANKYU, Yuji WADA, and Shozo YANAGIDA*
Chemical Process Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565

Photocatalytic fixation of CO_2 into benzophenone has been achieved under $\lambda >$ 400-nm light irradiation of a CO_2-saturated DMF solution of colloidal CdS microcrystallites as photocatalysts, triethylamine as a sacrificial electron donor, and benzo phenone yielding benzilic acid with benzhydrol and benzopinacol.

Photochemical fixation of CO_2 into organic compounds under visible-light irradiation has attracted substantial attention in terms of artificial photosynthesis.2) Although there are a few papers dealing with semiconductor-catalyzed photofixation of CO_2 into organic compounds using enzymatic electron relays,3) non-enzymatic fixation of CO_2 was not attempted. Recently, we have clarified that colloidal CdS microcrystallites (CdS-0, mean diameter = 4-nm, cubic) prepared at 0 °C from methanolic $Cd(ClO_4)_2$ and Na_2S solutions catalyze effective photoreduction of aromatic ketones with triethylamine (TEA) as a sacrificial electron donor.4) Interestingly, the sequential two-electron transfer reductions yielding alcohols are effectively induced after photoformation of lattice Cd^0 on CdS-0, and the one-electron transfer reductions yielding pinacols prevail when the formation of lattice Cd^0 was suppressed by the addition of an excess of sulfide ion in the system. On the other hand, another colloidal CdS microcrystallites (CdS-DMF, mean diameter = 4-nm, hexagonal) prepared at 0 °C from $Cd(ClO_4)_2.6H_2O$ and H_2S in DMF catalyze effective photoreduction of CO_2 to CO with TEA without photo-producing lattice Cd^0 on the photocatalyst. With these facts in mind, we aimed at photofixation of CO_2 into benzophenone (BP) by using such CdS photocatalysts. It has now been found that photofixation of CO_2 into BP can be achieved by using CdS-DMF as shown in Eq. 1.



(1)

Examined colloidal CdS photocatalysts (CdS-DMF, CdS-AN, and CdS-MeOH) and commercially available bulk CdS photocatalysts (CdS-Ald) are identical in previous papers.1,4) At first, we carried out a photolysis of BP with CO_2 using CdS-DMF and TEA. A small quantity of benzilic acid was detected. However, we found that pre-irradiation of the CdS system with no addition of BP is favorable for the photofixation of CO_2 into BP as shown in Table 1. Accordingly, photofixation was generally carried out as follows; a CO_2-saturated DMF solution (2 cm^3) containing CdS-DMF as photocatalysts (CdS diatomic concentration = 2.5×10^{-3} mol dm^{-3}) and TEA (1 mol dm^{-3}) as a sacrificial electron donor was closed with a rubber stopper, and then pre-irradiated with a 300 W tungsten halogen lamp through a sodium nitrite solution filter(λ >400 nm) with stirring. After 1-12 h pre-irradiation, BP (5 μmol) was added into the photolysate, and

Table 1. Photocatalytic Fixation of CO_2 into Benzophenone in CdS / TEA Systems

Run	Cat.	Solv.	Pre-irrad. time / h	React. time / h	Convn. /%	Product yield / %[a)] Benzilic acid	BPOH	$(BPOH)_2$
1	CdS-DMF	DMF	0	0.5	100	3.8	trace	30
2	CdS-DMF	DMF	1	0.5	100	8.5-12	8.5-10	15-24
3	CdS-Ald[b)]	DMF	12	6	50-52	0-0.2	0-2.9	65-69
4	CdS-AN	AN	2	2	100	0	81-88	trace
5	CdS-MeOH	MeOH	2	2	100	0	2.9-3.1	77-79

a) Yields are calculated on the basis of the substrate converted. b) CdS-Ald(hexagonal, mean diameter = 1.5 μm, 99.999%) was purchased from Aldrich. CdS-Ald(50 μmol) was used as photocatalysts.

further irradiated for 0.5–6 h. Photoproducts were analyzed by HPLC (for benzilic acid, BP, BPOH, and $(BPOH)_2$), and GC (for CO and H_2).

As a result, benzilic acid was formed in about 10% yield with benzopinacol ($(BPOH)_2$) and benzhydrol (BPOH) when CdS–DMF was used as a photocatalyst. As gas phase products, small quantities of CO and H_2 were also detected. As an oxidation product, diethylamine (DEA) was detected during photocatalysis, which is explained to be formed by hydrolysis of the initial oxidation product, $[Et_2NCHMe]^+$.4) In order to clarify the photofixation of CO_2 into BP, the photoreaction was carried out by using $^{13}CO_2$, and the reaction mixture was analyzed by ^{13}C–NMR. The signal at 177 ppm clearly suggested that $^{13}CO_2$ should be photofixed at the carbonyl carbon of BP, yielding benzilic acid. The reaction was extended to other active CdS photocatalysts under comparable conditions and the results are summarized in Table 1. Highly pure bulk CdS–Ald gave a trace of benzilic acid with exclusive formation of $(BPOH)_2$. However, colloidal CdS–AN prepared in acetonitrile gave only BPOH. On an examination of the photoreactions with CdS–AN, the darkening of colloidal CdS solution was observed during the photolysis, suggesting that the formation of Cd^0 should be favorable for the two–electron transfer reduction of BP to BPOH, but not for the photofixation of CO_2 into BP.4) In addition, CdS–MeOH and CdS–AN are not effective for the photoredcution of CO_2 to CO.1) These results imply that benzilic acid is formed through coupling between anion radical of CO_2 and the ketyl radical which are formed by one–electron transfer reduction. In other words, a direct reaction of intermediary anion radicals from BP with CO_2 seems improbable as an alternative mechanism, although such mechanism was proposed for the reductive photocarboxylation of aromatic hydrocoabons.5)

In conclusion, this is the first observation of non–enzymatic photofixation of CO_2 into an organic molecule catalyzed by the colloidal semiconductor.

References

1) Semiconductor Photocatalysis. Part 14; M. Kanemoto, K. Ishihara, Y. Wada, H. Mori, T. Sakata, and S. Yanagida, Chem. Lett., **1992**, 835.

2) I. Willner and B. Willner, Top. Curr. Chem., **159**, 157(1991).

3) D. Mandler and I. Willner, J. Chem. Soc., Perkin Trans. 2, **1988**, 997; H. Inoue, Y. Kubo, and H. Yoneyama, ibid., Faraday Trans., **87**, 553(1991).

4) T. Shiragami, H. Ankyu, S. Fukami, C. Pac, and S. Yanagida, J. Chem. Soc., Faraday Trans., **88**, 1055(1992).

5) S. Tazuke, S. Kazama, and N. Kitamura, J. Org. Chem., **51**, 4548(1986).

(Received July 2, 1992)