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Visible-light Induced Photocatalytic Fixation of CO_2 into Benzophenone Using Poly(*p*-phenylene) as a Photocatalyst

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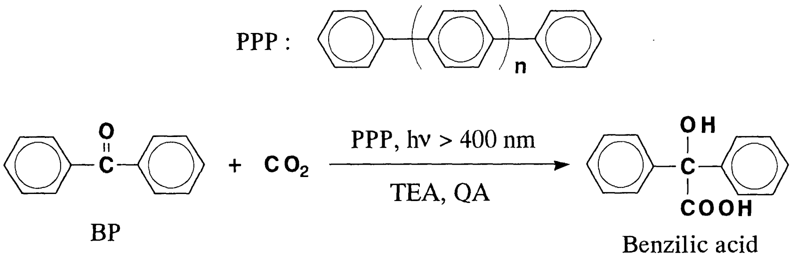
Photoreductive fixation of CO_2 into benzophenone can be achieved in a CO_2-saturated DMF solution by using poly(*p*-phenylene) as a heterogeneous photocatalyst and triethylamine as an electron donor. The presence of quaternary ammonium salts increases the yield of benzilic acid as a CO_2-photofixed product from benzophenone.

Some efforts have recently been conducted toward development of photochemical fixation of CO_2 into some organic molecules by using photosensetizers or photocatalysts.$^{1)}$ Recently, we reported that colloidal CdS microcrystallites prepared from cadmium salt and H_2S in DMF (CdS-DMF) catalyze not only photoreduction of CO_2 to CO but also photofixation of CO_2 into benzophenone yielding benzilic acid.$^{2)}$ The photofixation was interpreted to proceed through coupling between the radical anion of CO_2 and the ketyl radical that is formed by one-electron transfer reduction of benzophenone, since only the nanoscale CdS microcrystallites that are efficient for photoreduction of both CO_2 and benzophenone are effective for the formation of benzilic acid. On the other hand, we also found that linear aromatic compounds such as oligo(*p*-phenylenes) (OPP-n) or poly(*p*-phenylene) (PPP) induce effective photoreduction of CO_2 to formate and CO under UV-light irradiation in the presence of triethylamine as a sacrificial electron donor.$^{3)}$ With these in view, we have successfully attempted photofixation of CO_2 into benzophenone by using PPP as a photocatalyst, triethylamine (TEA) as an electron donor, and quaternary ammonium salt (QA) as a co-catalyst. The outline of this heterogeneous photofixation system is shown in Eq. 1.



(1)

As a photocatalyst, PPP was prepared according to a literature.$^{4)}$ Photoreaction was carried out as follows; in a Pyrex tube (8 mm in diameter) were placed PPP (10 mg), DMF solution (2 ml) of benzophenone (2.5 mM, 1 M = 1 mol dm^{-3}), distilled TEA (1 M) and quaternary ammonium salt (40 mM or none). After being purged with CO_2 gas, the tube was closed with a rubber stopper and then irradiated under stirring at $\lambda > 400$ nm using a 300 W tungsten halogen lamp and a sodium nitrite solution filter. Photoproducts were analyzed by GC (for CO and H_2), HPLC (for BP, BPOH, and $(BPOH)_2$), and three-dimensional HPLC (for benzilic acid). After an

Table 1. PPP-catalyzed Photofixation of CO_2 into Benzophenone in the Presence of Various Salts in DMF[a)]

Run	Additive[b)]	Convn / %	Product yield / %[c)]		
			Benzilic acid	BPOH	$(BPOH)_2$
1	None	100	3	6	37
2	Et_4NCl	100	34	3	34
3	Et_4NClO_4	100	16	6	38
4	n-Bu_4NCl	96	15	5	37
5	LiCl	100	5	8	25
6	$MgCl_2$	100	2	6	42

a) Irradiated at $\lambda > 400$ nm for 24 h. b) Each concn was 40 mM. c) Yields are calculated on the basis of converted benzophenone.

irradiation of a CO_2-saturated DMF solution containing only PPP, benzophenone, and TEA, a small quantity of benzilic acid (in less than 5% yield) was formed with benzopinacol ($(BPOH)_2$) and benzhydrol (BPOH). A trace amount of CO was also detected. However, it was found that an addition of tetraethylammonium chloride (Et_4NCl) into this photoreaction system improves the yield of benzilic acid (more than 30%). As an oxidation product, diethylamine (DEA) was detected during photoreaction, which is explained to be formed by hydrolysis of the initial oxidation product, $[Et_2NCHMe]^+$. The formation of other calboxylic acids (*e. g.*, $HCOO^-$, CH_3COO^-) was under the limit of detection by HPLC analysis using an anion-exclusion column. The photofixation of CO_2 into benzophenone was also confirmed by ^{13}C NMR analysis of the photoreaction which was carried out by using $^{13}CO_2$. The ^{13}C NMR spectrum was found to contain a signal at $\delta = 175$ ppm attributable to $^{13}COOH$ group of benzilic acid. These findings suggest that benzilic acid should be formed by the photofixation of CO_2 into benzophenone.

In Table 1 are summarized the results of photofixation of CO_2 into benzophenone in the presence of various salts. Et_4NCl was the most effective, while tetraethylammonium perchlorate (Et_4NClO_4) and tetrabutylammonium chloride (n-Bu_4NCl) were fairly effective. On the other hand, inorganic salts such as LiCl and $MgCl_2$ had almost no effects on the formation of benzilic acid.

Although the PPP-catalyzed CO_2 photoreduction to formate under visible light irradiation was not affected at all by the presence of Et_4NCl, the similar but homogeneous CO_2 reduction induced by p-terphenyl (OPP-3) under UV light irradiation, has become efficient in the presence of Et_4NCl. Further, the lifetime of the intermediary radical anion of OPP-3 has been observed to increase by a factor of 1.2 when compared with that in the absence of Et_4NCl.[5)] Further investigations on the role of quaternary ammonium salt in the heterogeneous photocatalysis of PPP are currently in progress.

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