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Photocatalysis of Oligo(*p*-phenylene) Leading to Reductive Formation of Hydrogen and Ethanol from Triethylamine in Aqueous Organic Solvent

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Oligo(*p*-phenylene)s, i.e., *p*-terphenyl to *p*-sexiphenyl, catalyze photoreductive formation of H_2 and ethanol in photolysis of aqueous solution of triethylamine under >290-nm irradiation in the presence of $RuCl_3$. *p*-Terphenyl shows unusually effective photocatalysis for the formation of ethanol in aqueous tetrahydrofuran even without $RuCl_3$.

We previously reported the photocatalysis of poly(*p*-phenylene) (PPP) for the reduction of water, ketones and olefins with triethylamine (TEA) as a sacrificial electron donor in the presence of Ru particles which formed by the concurrent photolysis of $RuCl_3$.1) These findings prompted us to know the minimum length of the *p*-phenylene chain for the photo-induced charge separation and the electron transfer. This paper reports that oligo(*p*-phenylene)s (OPP-n, n=3-6) primitively show the photocatalytic activity under UV light (>290 nm) toward water and acetaldehyde.

As reported in the PPP-catalyzed photoreaction, distilled water, TEA, methanolic $RuCl_3$ solution (6×10^{-3} mol dm^{-3}) (each 0.5 cm^3), and 10 mg of each OPP-n or PPP (synthesized by Yamamoto's method3)) were placed in a Pyrex tube (8 mm in diameter). After purging with argon gas, the tube was closed off with a gum stopper, and irradiated under magnetic stirring for 6 h at >290 nm using a 500 W high-pressure mercury arc lamp. The inner gas and liquid products were analyzed by GLPC as reported.1)

We have now found that OPP-n starting from *p*-terphenyl exhibit photocatalysis for the photoreduction not only of $RuCl_3$ to Ru^0 and water to H_2 but also of the concomitantly formed acetaldehyde to ethanol as follows (Table 1);

$$\text{OPP-n} \xrightarrow{h\nu} \text{OPP-n (e + h)} \qquad RuCl_3 \xrightarrow{e} Ru^0 \qquad H_2O \xrightarrow{e/Ru^0} H_2$$

$$(Et)_2NCH_2CH_3 \xrightarrow[-H^+]{2h} (Et)_2N^+CHCH_3 \xrightarrow[-(Et)_2NH]{OH^-} CH_3CHO \xrightarrow{2e,\,2H^+} CH_3CH_2OH$$

Since OPP-n (n=4-6) are almost insoluble in the reaction systems, the photocatalysis must work heterogeneously. The catalysis for the formation of H_2 tends to increase with the number of the phenylene unit. It is noteworthy, however, that photocatalysis of OPP-3 led to the most effective formation not only of H_2 but also of ethanol. The OPP-3-catalyzed photoreduction of D_2O gave D_2, DH, and H_2 in a 51 : 38 : 11 ratio, indicating that the major source of H_2 is water.

Table 1. OPP-Catalyzed Photolysis of TEA in the Presence of $RuCl_3$

Catalyst	Absorption[a] λ_{max}/nm	Solubility[b] g cm^{-3}	Photoproduct[c] / μmol H_2	DEA[d]	Ethanol
OPP-2	245	(440)	0.8	-	-
OPP-3	283	0.28 (8.5)	5.9	42	29
OPP-3		>1.0[e]	40[e]	173[e]	94[e]
OPP-4	300	<0.01 (0.22)	1.0	14	1.2
OPP-4			5.7[e]	18[e]	4.6[e]
OPP-5	311	<0.01 (<0.1)	1.6	20	2.0
OPP-6	316	<0.01 (<0.01)	2.8	22	2.0
PPP	425[f]	≒0	54	87	6.5

a) Measured in THF. b) In methanol at 20 ℃. In parentheses is each solubility in toluene.[3] c) After irradiation at >290 nm for 6 h. d) Diethylamine. e) In aqueous THF. f) Band gap.[1]

Taking into account fair solubility of OPP-3 in methanol, the photolysis with OPP-3 or OPP-4 was carried out in aqueous THF where OPP-3 and OPP-4 are still more soluble. As shown in Table 1, more effective photoredox reactions were observed for OPP-3 and OPP-4. In OPP-3-catalyzed photoreactions, the formation of Ru^0 particles (ca. 70 nm) was confirmed by direct TEM observation. Interestingly, OPP-3 was found still effective for the formation of ethanol in the photolysis without $RuCl_3$ (Fig. 1). These observations suggest that the dissolved OPP-3 should play an effective role in both photooxidation of TEA and photoreduction of acetaldehyde to ethanol and that R^0 formed in OPP-n systems should work as electron relays for the reduction of water in the same way as in some photocatalyses.[1,4] Further studies on the noble photo-induced charge separation on OPP-n are in progress.

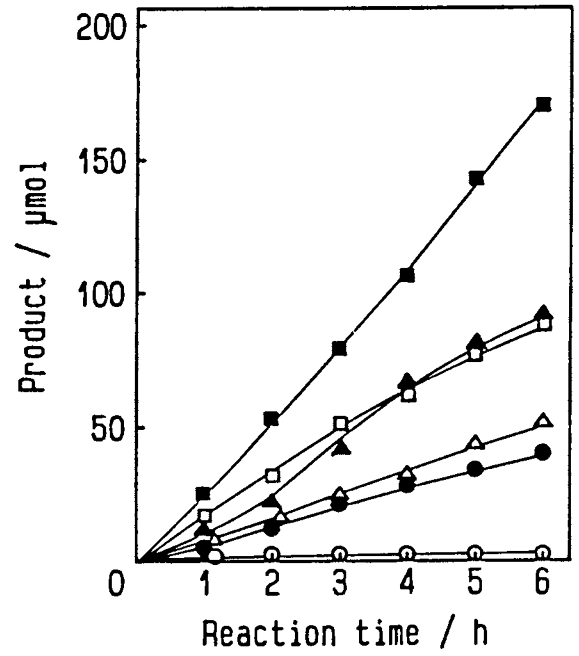

Fig. 1. OPP-3 Catalyzed photolysis of triethylamine in aqueous THF: with $RuCl_3$, (●) H_2, (▲) EtOH, (■) DEA; wihtout $RuCl_3$, (○) H_2, (△) EtOH, (□) DEA.

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