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A Novel Photo-induced Fenton's Reaction. Perfluorinated Poly(*p*-Phenylene)-catalyzed Photohydroxylation of Benzene with O_2 and H_2O to Phenol

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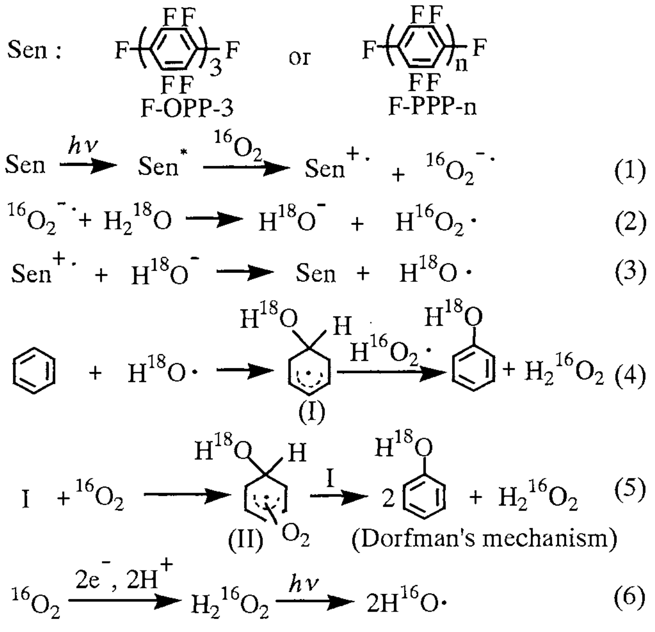
^{18}O Tracer study of perfluorinated poly(*p*-phenylene)-catalyzed photohydroxylation of benzene to phenol with $H_2{}^{18}O$ and $^{16}O_2$ revealed that the hydroxylation initially occurs by the attack of the hydroxyl radical ($H^{18}O\cdot$) generated by the photooxidation of $H_2{}^{18}O$, but the hydroxyl radical ($H^{16}O\cdot$) derived from the concurrently produced $H_2{}^{16}O_2$ comes to participate in further hydroxylation as the photocatalysis proceeds.

In the preceding paper,[1] we reported that perfluorinated *p*-terphenyl (F-OPP-3) catalyzes the photooxidation of benzene to phenol in the presence of O_2 and H_2O upon UV (λ>290 nm) irradiation, and proposed a mechanism through the F-OPP-3-catalyzed photooxidation of hydroxide ion (HO^-), leading to hydroxycyclohexadienyl radical (I) (Scheme 1, Eq. 1-4), because an equimolecular amount of H_2O_2 was produced concurrently with phenol and the presence of H_2O was a requisite for the photoreaction. On the other hand, the role of oxygen in the hydroxylation of benzene with Fenton's reagent was studied recently[2] and the reaction of I with O_2 was confirmed to result in the regeneration of H_2O_2 from peroxy radical (II) (Dorfman's mechanism), which can be regarded as reduction of O_2 with I (Scheme 1, Eq. 5). It is also known that the photolysis of H_2O_2 with benzene and oxygen upon λ>290-nm-irradiation yields phenol and hydroxymucondialdehyde derivatives due to the photoformation of $HO\cdot$ (Scheme 1. Eq. 6).[3]

In order to confirm the photooxidation of water and to clarify the contribution of $HO\cdot$ from H_2O_2 to the photo-hydroxylation, ^{18}O isotope incorporation in phenol was examined in the F-OPP-3 photosystem. The photohydroxylation of benzene was carried out under the same conditions as in the preceding studies using $^{16}O_2$ and $H_2{}^{18}O$ (99.8%). The isotope incorporation was examined by GC-MS analysis, the intensity of the molecular ion peaks of $C_6H_5{}^{18}OH$ and $C_6H_5{}^{16}OH$ being monitored during the photocatalysis. Each ratio of



(Photocatalytic reduction and / or Dorfman's mechanism, and photolysis)[4]

Scheme 1.

$C_6H_5{}^{18}OH$ to that of $C_6H_5{}^{16}OH$ is summarized in Table 1. The largest value was obtained at the beginning of the photolysis and the ratio decreased as the photolysis proceeded. The gradual change in the ratio strongly suggests that $H^{18}O\cdot$ produced by the photooxidation of $H^{18}O^-$ should play an important role in the initial hydroxylation of benzene, but $H^{16}O\cdot$ from $H_2{}^{16}O_2$ gradually prevails. The isotope scrambling in phenol should occur through the HO· formation (Scheme 1. Eq.6). Furthermore, to clarify the similarity with the hydroxylation using Fenton's reagent in the presence of O_2,[2,5] the photohydroxylation with perfluorinated poly(*p*-phenylene) (F–PPP–n, n=3–10) was studied (conditions; F–PPP–n, 1.0 mg, Benzene, 0.4 cm^3; H_2O; 0.04 mg, O_2 saturated acetonitrile, 1.56 cm^3).[1b] The heterogeneous photocatalysis using F–PPP–n showed enhanced photoproduction of phenol compared to F–OPP–3 and F–OPP–4, the phenol formation leveling off after 3–h irradiation (Fig. 1). ^{18}O Incorporation in phenol was also ascertained at the early stage of the photocatalysis (Table 1). HPLC analysis (cosmosil (nacalai tesque), φ 4.6 mm x 25 cm; acetonitrile–phosphate buffer, 1:4 v/v) of the photolysate revealed that very small quantities of 1,2,4–trihydroxybenzene, hydroquinone and benzoquinone (about 10% of phenol produced) were formed together with other unidentified byproducts, which were speculated to be mainly hydroxymucondialdehydes based on their retention volume being identical with those of the peaks observed in the photolysis of benzene with H_2O_2.[3] The leveling–off in the formation of phenol after 3–h irradiation can be ascribed to the coloration (pale yellow) of the photolysate. To our knowledge, this is the first example of heterogeneous Fenton's reaction photo–induced with organic molecules, H_2O, and O_2.

Table 1. Ratio of the Intensity of the Molecular Ion Peak of $C_6H_5{}^{18}OH$ to $C_6H_5{}^{16}OH$ in the Reaction System with F-OPP-3 or F-PPP-n

	$C_6H_5{}^{18}OH / C_6H_5{}^{16}OH$	
Time / min	F-OPP-3	F-PPP-n
20	-	3.47
40	1.92	1.77
60	1.64	1.39
80	1.34	1.12
100	1.08	1.10
120	0.82	0.85
180	0.53	0.58

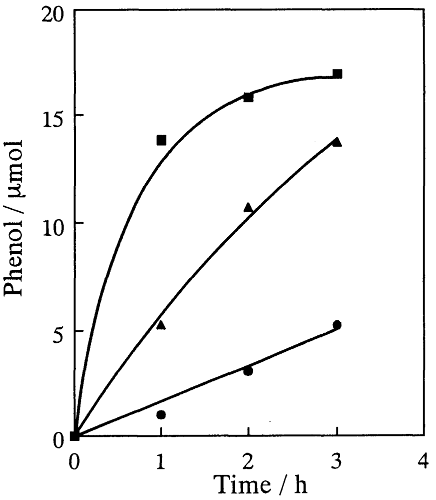


Fig. 1. Perfluorinated *p*-phenylenes-catalyzed photooxidation of benzene to phenol with O_2 and H_2O in acetonitrile : (●) F-OPP- 3; (▲) F-OPP-4; (■) F-PPP-n.

References

1) a) K. Maruo, Y. Wada, and S. Yanagida, *Bull. Chem. Soc. Jpn.*, **65**, 3439 (1992); b) K. Maruo, Y. Wada, and S. Yanagida, *Bull. Chem. Soc. Jpn.*, in press.

2) A. Kunai, S. Hata, S. Ito, and K. Sasaki, *J. Am. Chem. Soc.*, **108**, 6012 (1986).

3) N. Jacob, I. Balakrishnan, and M. P. Reddy, *J. Phys. Chem.*, **81**, 17 (1977).

4) The coexistence of F–PPP–n did not increase the rate of photohydroxylation of benzene with H_2O_2, which suggests few contribution of HO· from $H_2O_2{}^{-\cdot}$ producible from F–PPP–n–catalyzed photoreduction of the generated H_2O_2.

5) M. Fujihira, Y. Satoh, and T. Osa, *Nature*, **293**, 206 (1981).

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