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PHOTOSENSITIZED DIMERIZATION OF PHENOL IN PORPHYRIN-QUINONE-PHENOL SYSTEM

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Photosensitized dimerization of 4-methoxyphenol was observed upon irradiation of porphyrin in the presence of quinone. Quantum yield for dimer was depended upon the concentration and reduction potential of quinones used. Free radical coupling mechanism was confirmed by means of ESR and CIDNP techniques.

Since Grossweiner et al. reported the flash photolysis on the photosensitized reaction of eosin with phenol in 1959,1) phenol compounds have been widely used as reductants in the photosensitized reaction of triplet dyes.2) In most cases, however, oxygen has been used as the oxidant and there has been usually observed no chemical changes under deaerated conditions because of reverse hydrogen atom transfer from phenol to triplet dyes. Xanthene and triphenylmethane dyes have been occasionally employed in photoreactions with phenols,3) although, porphyrin compounds, a class of the representative dyes, have been rarely used with the exception of the oxygenation reaction by singlet oxygen.4)

On the other hand, considerable attention has recently been focused on the photo-induced reactions of porphyrins with quinones as simple models for photosynthesis.5) However, most of light-energy absorbed by porphyrins is consumed by the rapid reverse electron transfer in the geminate radical ion pair, porphyrin cation radical and quinone anion radical, resulting no stable products formation likewise with the case of porphyrin-phenol system. In this paper, we will report the accumulation of stable products in the photoreaction of the three-components-system involving sensitizer (porphyrin), electron donor (phenol) and electron acceptor (quinone).

When a mixture of 5,10,15,20-tetraphenylporphyrin (5×10^{-4} M), 4-methoxyphenol (1) (1×10^{-1} M) and p-benzoquinone (Q) (1×10^{-2} M) dissolved in benzene was irradiated under argon atmosphere with a light of wavelength longer than 590 nm, resulted in the formation of phenol dimer, 2-hydroxy-4',5-dimethoxy-diphenylether (2) in a yield of 49%, along with hydroquinone (H_2Q) at 50% conversion of Q. TPP remained unchanged at this stage of the reaction. The regioselective coupling at 2-position of 1 was unambiguously confirmed by 400 MHz ^{1}HNMR and GLC analysis. As the reaction proceeded, the rate of product formation decreased markedly probably because of the accumulation of H_2Q acting as radical scavenger.$^{6)}$ When H_2Q (1×10^{-2} M) was added to a standard solution prior to irradiation, the dimerization of 1 did not occur at all. These scavenging effects of H_2Q indicate that the dimerization takes place via free radical processes. Actually, free 4-methoxyphenoxy radical was detected at a room temperature by ESR ($g=2.0052$, $a^{o}=5.51$ G and $a^{m}=0.75$ G)$^{7)}$ during the reaction. Further, by ^{1}H-CIDNP experiment, we realized emission polarized signal of Q along with substantial broadening signals due to ring hydrogens and hydroxyl group of 1. This is a clear indication of a reasonably high accumulation of free 4-methoxyphenoxy radical during the reaction.

Quantum yield (Φ_d) for the formation of the dimer 5 was dependent upon the concentrations of both 1 and Q (Figs. 1 and 2). Φ_d increased with higher concentration of 1, while Φ_d reached at a maximum at $[\,Q\,] = 6\times10^{-3}$ M and then decreased markedly with increasing concentration of Q. The profile of Φ_d dependent upon Q given in Fig.2 well coincides with that of porphyrin triplet yield calculated by using porphyrin fluorescence quenching data,$^{9)}$ clearly indicating that present reaction takes place via porphyrin triplet state.

A variety of benzoquinone derivatives other than Q were employed as oxidants in this photo-induced dimerization of 1. As shown in Fig.3, Φ_d was greatly dependent upon the reduction potentials of quinones used. Larger Φ_d values were observed with use of halogenoquinones of lower reduction potentials, whereas with alkylsubstituted benzoquinones no dimerization did occur. Since oxidation potential of TPP triplet, $^3TPP^*$, $E(TPP^{\cdot+}/^3TPP^*)$ was reported to be -0.51 V (vs. s.c.e.),$^{10)}$ and reduction potential of Q $E(Q/Q^{\cdot-})$ to be -0.51 V,$^{11)}$ electron transfer from TPP triplet to quinone should be unfavorable in the case

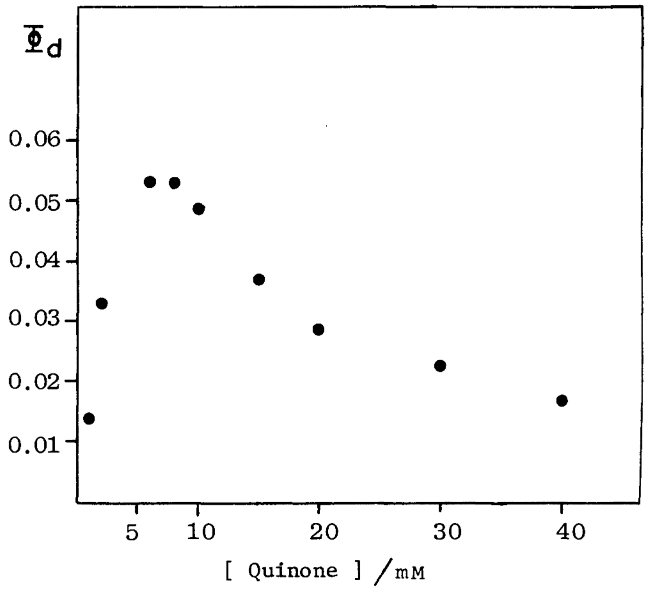


Fig. 1. Dependence of Quantum Yield (Φ_d) for Formation of Photo-induced Coupling Dimer upon Concentration of Benzoquinone.
[TPP] : 0.1 mM. [4-Methoxyphenol] : 100 mM.

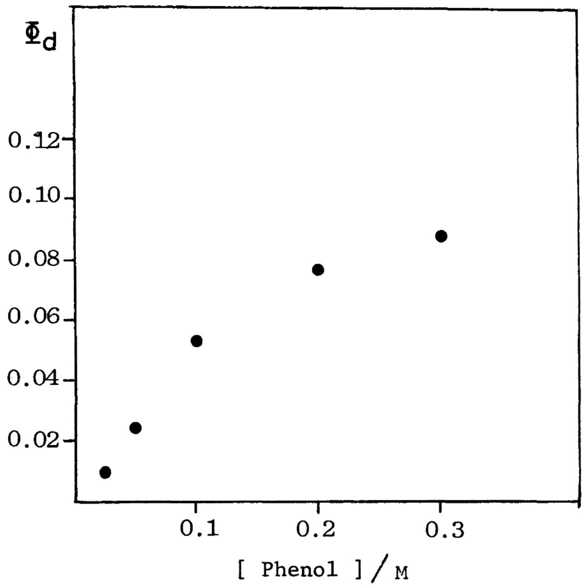


Fig. 2. Dependence of Quantum Yield (Φ_d) for Formation of Photo-induced Coupling Dimer upon Concentration of 4-Methoxyphenol.
[TPP] : 1x10^{-4} M. [Benzoquinone] : 5x10^{-3}M.

of the alkyl-substituted benzoquinones (RQ) with higher reduction potentials than Q. Actually, with use of substituted meso-porphyrin dimethyl ester, whose reduction potential was supposed to be -0.56 V,$^{10)}$ in this photoreaction with (RQ), only a moderate yield of 2 was observed (Φ_d = 0.02-0.05). Possible mechanisms for the dimerization can be depicted as shown in Scheme 1. Oxidative quenching of $^3TPP^*$ by Q may lead to the formation of a radical ion pair, $\overline{TPP^{+}\cdot Q^{-}\cdot}$, which could regenerate the starting materials by reverse electron ransfer in the absence of 1. In the presence of 1, however, the radical ion pair reacts with 1 to give 4-methoxyphenoxy radical and semiquinone radical HQ . The former gives 2, while the latter decays mainly by disproportionation. An alternative mechanism involving reductive quenching of $^3TPP^*$ by 1 followed by electron transfer from $TPP^{-\cdot}$ to Q may be conceivable. However, under our conditions with [1]= 1x10^{-1} M and [Q]= 1x10^{-2} M, about 95% of $^3TPP^*$ is estimated to be quenched by Q on the basis of their quenching rates of $^3TPP^*$.$^{12)}$ Therefore , it may be safely considered that the oxidative mechanism is responsible for the major reaction course.

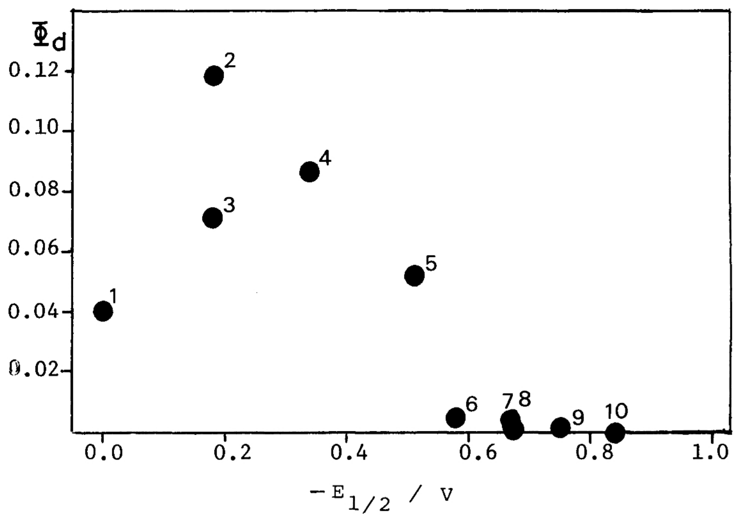
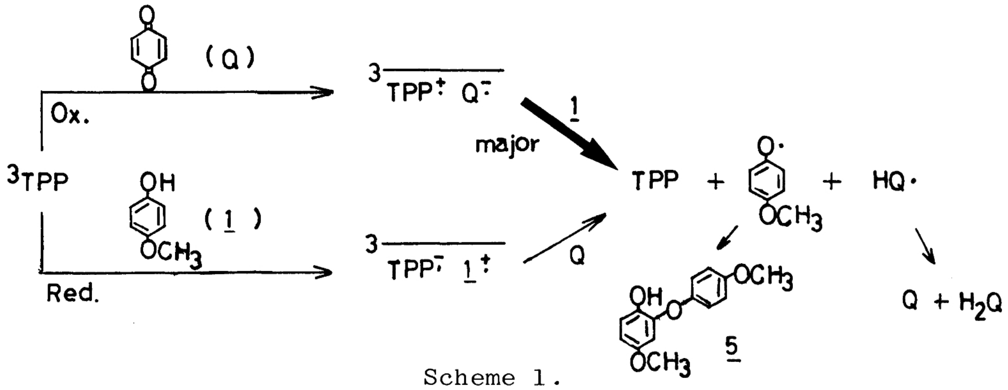


Fig. 3. Dependence of Quantum Yield (Φ_d) on the Reduction Potential of Quinones.
Quinones used are : chhloranil (-0.01)[1]; 2,5-dichloroquinone (0.18)[2]; 2,6-dichloroquinone (0.18)[3]; chlorobenzoquinone (0.34)[4]; benzoquinone (0.51)[5]; toluquinone (0.58)[6]; 2,5-dimethylbenzoquinone (0.67)[7]; 2,6-dimethylbenzoquinone (0.68)[8]; trimethylbenzoquinone (0.75)[9]; and duroquinone (0.84)[10]. In parenthesis are indicated the reduction potentials vs. s.c.e.. (Ref. 11).



Scheme 1.

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