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Redox Reaction of the Central Metal Ions Coordinated to Tetra(*p*-sulfophenyl)porphine (TPPS). II. Photoreduction of $[Fe(III)TPPS]_2O$ by Ethanol

Keiichiro Hatano* and Yoshitaka Ishida
Department of Pharmaceutical Sciences, Nagoya City University, Mizuho-ku, Nagoya 467

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Synopsis. Iron(III) ion coordinated to TPPS was reduced to the divalent ion by ethanol on illumination of light. The reaction rates appear to obey the half-order kinetic of the metalloporphyrin in the buffered solutions of pH 7 to 11. A possible reaction mechanism is discussed.

The photochemical redox behavior of metalloporphyrins is of continuing interest due to their biomimetic functions as chlorophylls in photosynthesis and their possibilities as photosensitizers for solar energy conversion. Besides our study of the photoreduction of Co(III)-TPPS,1) some recent work that is relevant to our present kinetic investigation of iron porphyrin photochemistry may be cited as follows: the photoreduction of Mn(III)-TPyP2) and the Mn(IV) derivatives by ethanol or water studied extensively by Harriman and Porter,3) and the photoreduction of hemin in ethanol–pyridine–water mixed solvents by Bartocci *et al.*4)

Dimer formation for Fe(III), Mn(III), or Mn(IV) porphyrin in basic solutions is certain,5) or at least suggested by the X-ray moleculer structures.6,7) The coordination of water or alcohols to these metalloporphyrins is certain from the crystal structures.8–10) This note describes some details of earlier data11) of the photoreduction of Fe(III)TPPS, here we treat the μ-oxo dimer formation and the axial ligation of ethanol.

Figure 1 shows typical spectral changes of Fe(III)-TPPS in the deaerated aqueous ethanol during the photolysis in two separate experiments. The changes can be ascribed to the photoreduction of the central iron(III) ion of FeTPPS to the iron(II) ion, judging from the spectral characteristic of the product Fe(II)-TPPS, and the reoxidation of it to the original Fe(III)-TPPS by air introduction. Fe(III)TPPS restored by a cycle of the redox reactions is, though dependent on the irradiation time and other conditions, almost quantitative (>95%) in regular experiments. Furthermore, acetaldehyde detected in the irradiated solution as the oxidation product of ethanol confirms that the overall reaction is an autoxidation reaction of ethanol catalyzed by the $Fe(III)\rightleftharpoons Fe(II)$ couple of FeTPPS. Some apparent isosbestic points are found in the spectral changes, but close inspection in the spectra reveals that the photochemical reaction is not a simple interconversion of Fe(II)- and Fe(III)TPPS but that some other minor species also take part. In particular, the spectrum of μ-oxo dimer in alkaline solution resembles closely that of the ethanol coordinated iron(III)-porphyrin species which are expected to be formed in the neutral aqueous solution with the addition of ethanol. Thus, several species having a similar absorption spectrum or very small abundance in the solution are considered to overlap into a spectrum represented by that of μ-oxo dimer. This situation does not allow the strict and accurate analysis of the reaction rates. However, the distinct absorption of Fe(II)TPPS in the Soret region and the known optical density can permit the plausible reaction mechanism elucidation unless the trace of spectra goes severely off from the quasi-isosbestic points in the spectral changes. The observed rates of the photoreduction fit approximately the following equation under the conditions of the constant photon flux and pH:

$$d[Fe(II)TPPS]/dt = k'[(FeTPPS)_2O]^{1/2}[ethanol].$$

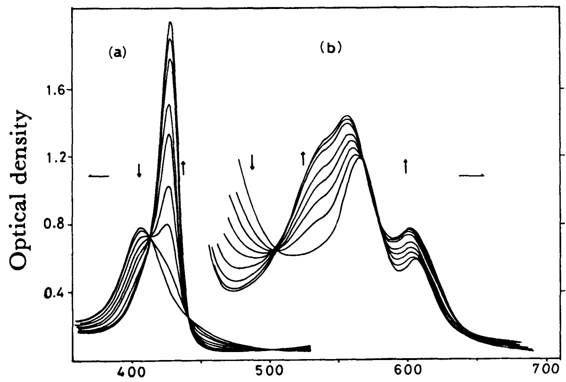

Fig. 1. Spectral changes of FeTPPS during photolysis. Experimental conditions and reaction times shown in the order of arrows are: (a) 3.8×10^{-6} M $(FeTPPS)_2O$, 2.5 M ethanol, at pH 8.0, and 0, 10, 20, 30, 45, 60, 90, 120, and 210 min. (b) 4.5×10^{-5} M $(FeTPPS)_2O$, 4.0 M ethanol, at pH 8.4, and 0, 10, 20, 30, 40, 55, 70, 90, 120 min. 1 M = 1 mol dm^{-3}.

Figure 2 demonstrates the half-order rate dependence in the metalloporphyrin kinetics. The half-order kinetic is also confirmed by the experiments varying the initial concentrations of Fe(III)TPPS. Fleischer *et al.*5) have studied the kinetics of the monomer-dimer equilibrium reaction of Fe(III)TPPS in aqueous

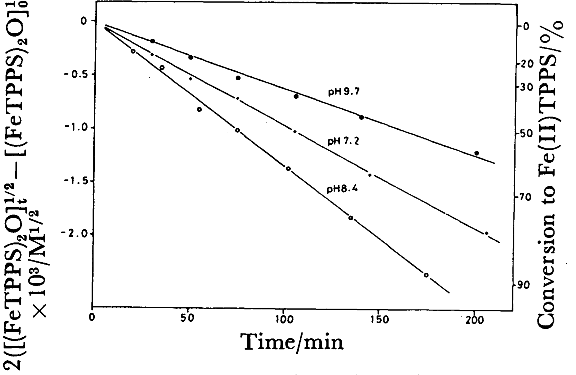

Fig. 2. The half-order rate dependence in $(FeTPPS)_2O$ kinetics at various pH. The right hand scale shows % conversion of $(FeTPPS)_2O$ to Fe(II)TPPS.

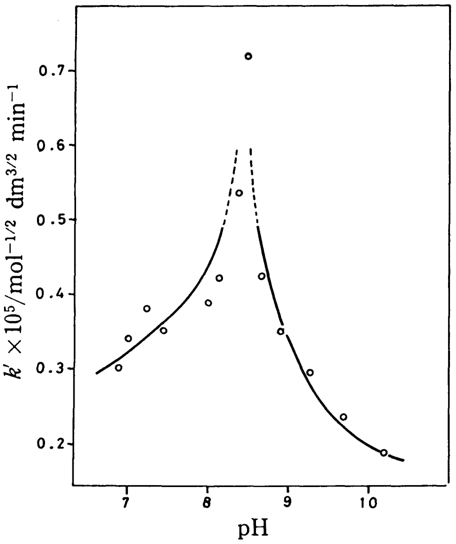

Fig. 3. The pH profile of the rate constants, k'. [Ethanol] $=2.5$ M.

solutions; the rate of the reaction is reported to be faster than that of the present photoreaction. Therefore, the rate-determining step of the photoreduction should not be the dissociation of dimer into monomer. The initial stage of the linkage chain hydrogen-bromine reaction has been classically analyzed as the half-order kinetic approximation in bromine concentration.[12] A similar interpretation can apply for the present reaction mechanism. Thus, a photoinduced electron transfer reaction is considered to be the rate-determining step involving a monomeric photosensitive species. The plausible representation of the reaction scheme to elucidate the kinetics is written as:

$$\mathrm{(FeTPPS)_2O + H_2O \rightleftarrows 2Fe(III)TPPS(OH)}$$

$$\mathrm{Fe(III)TPPS(OH) + C_2H_5OH \rightleftarrows Fe(III)TPPS(OH)(C_2H_5OH)}$$

$$\mathrm{Fe(III)TPPS(OH)(C_2H_5OH) \xrightarrow{h\nu} Fe(II)TPPS + CH_3\dot{C}HOH + H_2O.}$$

The first-order kinetic in ethanol concentrations substantiates the coordination of one ethanol molecule to a photosensitive ferric species. The mechanistic representation is principally identical to the photoreduction of Co(III)TPPS.[1] The entity of the particular ternary complex coordinating an OH ion as the photosensitive species is supported by the kinetic studies in solutions of varying pH. As shown in Fig. 3, the volcano-shape profile of the rate constants, k', against pH indicates that there is an optimal concentration of hydroxide ion to stabilize the photosensitive species.

The overall quantum yield depends on the quantity of the photosensitive species in solutions. The highest observed quantum yield (*ca.* 0.01) is achieved at high ethanol concentration (5.2 M), optimal pH (8.5), and relatively low concentration of FeTPPS (1.6×10^{-6} M). The pursuit of higher values is hampered by the low solubility of FeTPPS in ethanol.

The reoxidation reaction occurs. The rate is too rapid to be followed by the traditional spectromeric device. This suggests that the reducing potential of Fe(II)TPPS is higher than that of Co(II)TPPS, toward the dioxygen molecule.

Experimental

FeTPPS was prepared as described.[5] Dark green powder was obtained by treatment of crude material in methanolic solutions with sodium methoxide several times. Found: C, 43.19; H, 3.04; N, 4.86; S, 10.57%. Calcd for $\mathrm{(FeTPPS\,Na_4)_2O\ 16H_2O}$, $\mathrm{C_{88}H_{80}N_8S_8O_{41}Fe_2Na_8}$: C, 43.01; H, 3.29; N, 4.56; S, 10.44%.

Procedures and instruments employed in the experiments were the same as reported previously[1] except that a Wacom XD-501S xenon lamp was also used. The quantum yield was determined by comparison of spectrometric measurements to the CoTPPS case. Acetaldehyde was analyzed in the sample distilled in vacuo from the FeTPPS solution photolyzed for 45 h using a qualitative *p*-phenylenediamine–$\mathrm{H_2O_2}$ method[13] and a nitroprusside method[13] as a quantitative detection. Although both methods are not specific for acetaldehyde, the negligible amount of the porphyrin decomposition and the normal quantum yield (10^{-3} order) for alcohol oxidation support this assignment.

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