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Photoreduction of Hydroxo(tetramesitylporphinato)iron(III) in Aromatic Hydrocarbons and the Concurrent Generation of Hydroxyl Radical

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Hydroxo(tetramesitylporphinato)iron(III) in degassed benzene, toluene, and ethylbenzene is confirmed to be reduced to the four coordinate ferrous complex upon irradiation with light λ>300 nm. Production of diphenyl and solvent dependence of photoreduction rates support the concurrent generation of hydroxyl radical along with the ferrous complex production.

The photochemistry of metalloporphyrin complexes has been the subject of recent extensive examinations.1) Among these are the investigations on the photochemical behavior of ferric heme complexes. Until recently, there are some reports on the photoreduction of the iron center.2,3) In the case of ferric heme with hydroxo axial ligand, however, its photoreducibility has not been confirmed as yet in a simple system which consists of hydroxo heme and non-coordinating solvent.

The unique properties of hydroxo heme complexes have receiving attention lately.4,5) The deliberate examination of these compounds became feasible owing to the availability of hindered porphyrins, which carry bulky substituents and are prevented from the conversion into μ-oxo-dimers. For the simplest example, hydroxo(tetramesitylporphinato)iron(III)(Fe^{III}(tmp)OH) is available.5)

In a preliminary experiment using deaerated toluene containing small amount of pyridine as a solvent, Fe^{III}(tmp)OH was found to be readily photoreduced to the bispyridine hemochrome. This result prompted us to examine photochemical behavior of Fe^{III}(tmp)OH in pure hydrocarbons under aerobic and anaerobic conditions. We wish to report in the present letter the photoreduction of Fe^{III}(tmp)OH in pure benzene, toluene, and ethylbenzene and discuss the concurrent generation of hydroxyl radical.

Fe^{III}(tmp)OH and Fe^{III}(tmp)Cl were prepared by literature procedure.5) Benzene, toluene, and ethylbenzene were distilled from sodium and stored over 4A molecular sieves. A reaction cell with two Pyrex glass cuvettes(10 and 1 mm pathlength) was used to take spectra of the same solution in both Soret and visible regions. After the cell was joined to a vaccum line, the solution contained was outgassed by the freeze-pump-thaw cycle. Irradiations were performed with a 500-W xenon lamp(Ushio) or a 200-W high-pressure mercury lamp(Nikko Sekiei) with a Pyrex glass filter which cuts off light $\lambda<300$ nm. Spectral changes were monitored in a Union Giken SM-401 spectrophotometer. All spectra shown here were automatically digitized as they were recorded, the appropriate baselines were subtracted, and the resulting spectra were replotted with a computer.

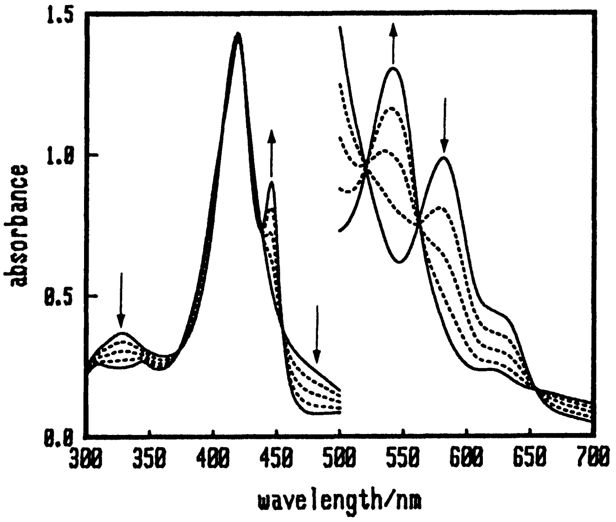

Fig. 1. Spectral change of Fe(tmp)OH in pure toluene upon irradiation for 0, 20, 90, 240, and 1080 s. The cell length was 10 mm and 1 mm for the 500-700 and 300-500 nm regions, respectively.

The deaerated toluene solution of $\mathrm{Fe^{III}(tmp)OH}$ (1.3×10^{-4} mol dm^{-3}) was irradiated with light $\lambda>300$ nm (Figure 1). The absorption band at 580 nm of $\mathrm{Fe^{III}(tmp)OH}$ was shifted to 540 nm, with the appearence of a new band at 446 nm, isosbestic points were found at 375, 410, 440, 456, 522, 563, and 658 nm. The final spectrum was almost identical to that of $\mathrm{Fe^{II}(tmp)}$ obtained by chemical reduction of $\mathrm{Fe^{III}(tmp)OH}$ or $\mathrm{Fe^{III}(tmp)Cl}$ with zinc amalgum (Zn(Hg)).[5)] The spectrum was characteristic of four coordinate "bare Fe(II) heme".[3,6)] On exposure to air, the photoreduction mixture changed immediately from pink to brown-green. This phenomenon accounts for the reproduction of $\mathrm{Fe^{III}(tmp)OH}$ by autoxidation of ferrous heme.[5)] It was thus proved that $\mathrm{Fe^{III}(tmp)OH}$ in degassed toluene was photoreduced to the four coordinate ferrous complex, $\mathrm{Fe^{II}(tmp)}$.

In the photoreduction process, the coordinated hydroxide anion must be considered to dissociate in a "radical form" from the axial coordination position. We have tried finding diphenyl in the irradiated benzene solution of $\mathrm{Fe^{III}(tmp)OH}$. Diphenyl is well known as an end product of the reaction of benzene with hydroxyl radical.[7)] The photoreaction mixture was chromatographed over silica gel with hexane as eluent to remove porphyrin species and the eluate was evaporated. The colorless crystalline residue was identified as diphenyl by comparing its TLC patterns and MASS, NMR, and UV spectra with those of an authentic sample.[8)] The yield based on the hydroxo heme was about 34%.

The driving force in $\mathrm{Fe^{II}(tmp)}$ production can be attributed to the power of the solvent to scavenge radical ·X which is generated as a result of the homolytic cleavage of Fe-X bond (Eqs. 1-3).[3)] We have evaluated the rate of $\mathrm{Fe^{II}(tmp)}$ production from $\mathrm{Fe^{III}(tmp)OH}$ or $\mathrm{Fe^{III}(tmp)Cl}$ in benzene, toluene, and ethylbenzene under anaerobic conditions (Table 1). In both cases of $\mathrm{Fe^{III}(tmp)OH}$ and $\mathrm{Fe^{III}(tmp)Cl}$, the rate of $\mathrm{Fe^{II}(tmp)}$ production has a strong solvent dependence. In the case of $\mathrm{Fe^{III}(tmp)Cl}$, the rate was decreased in the order: ethylbenzene>toluene>benzene;

$$\mathrm{Fe^{III}(tmp)X} \longrightarrow \mathrm{Fe^{II}(tmp)} + \cdot\mathrm{X} \qquad (1)$$

$$\mathrm{Fe^{II}(tmp)} + \cdot\mathrm{X} \longrightarrow \mathrm{Fe^{III}(tmp)X} \qquad (2)$$

$$\cdot\mathrm{X} + \text{solvent} \longrightarrow \text{products} \qquad (3)$$

Table 1. Rates of $Fe^{II}(tmp)$ production from $Fe^{III}(tmp)Cl$ or $Fe^{III}(tmp)OH$ upon irradiation a)

Solvent	Time required for 50% photoreduction b)	
	$Fe^{III}(tmp)Cl$	$Fe^{III}(tmp)OH$
benzene	very long c)	20 s
toluene	1.5 h	260 s
ethylbenzene	41 s	12 s

a) $[Fe(tmp)Cl]_0=[Fe(tmp)OH]_0=5.6\times10^{-5}$ mol dm^{-3}; T=20 °C

b) Photoreduction degree was determined by using the spectrum of Fe(tmp) obtained by chemical reduction of Fe(tmp)Cl with Zn(Hg).

c) Almost unchanged after 2 h.

the lower the C-H bond energies of the solvents are, the higher the rates of $Fe^{II}(tmp)$ production are.3) This is consistent with the abstraction of the hydrogen atoms from the solvents by the chloro radicals as a key step in the overall photoreduction of $Fe^{III}(tmp)Cl$. However, in the case of $Fe^{III}(tmp)OH$, the rate was decreased from ethylbenzene to benzene to toluene; the parallel relation does not exist between the photoreduction rates and the solvents' bond dissociation energies. These results are in favor of the concurrent generation of hydroxyl radical in the photoreduction process of $Fe^{III}(tmp)OH$. Distinct differences in the solvent dependences result from differences between hydroxyl radicals and chloro radicals in the manner in which the radicals are scavenged by the solvents. In fact, hydroxyl radical is known to react with benzene or substituted benzenes predominantly by addition to the ring and not by abstraction of hydrogen atom.9) Moreover, the formation of hydroxycyclohexadienyl radical, resulting from the addition of hydroxyl radical to the benzene ring, must complicate the situation.10) From the above results, it appears well established that hydroxyl radicals are generated along with four coordinate $Fe^{II}(tmp)$ in the photoreduction process in benzene.11)

When irradiated under aerobic conditions, the benzene solution gradually bleached. After the solution had become unchanged further, diphenyl generated in the solution was isolated and determined spectrophotometrically. The yield was about 15 times that under anaerobic conditions. These results must be interpreted as follows: $Fe^{II}(tmp)$ formed in the solution is reoxidized by the atmospheric dioxygen to $Fe^{III}(tmp)OH$,5) which is again photoreduced to $Fe^{II}(tmp)$. During this reaction cycle, hydroxyl radicals are successively generated. These hydroxyl radicals react with benzene to produce diphenyl. On the other hand, they also attack the porphyrin rings to result in the rupture of the chromophore.

In sum, a clear photoreduction phenomenon was observed in a very simple system which consists of only hydroxo ferric heme and aprotic solvent. Therefore, the present system might offer fundamental data for detailed study of the photoreducibility of more complicated system, for example, hemeprotein in various buffer solutions.12) Further, the present system is regarded as an efficient photocatalyst that generates hydroxyl radicals under aerobic conditions, since $Fe^{II}(tmp)$ is reoxidized to the starting material($Fe^{III}(tmp)OH$) without the formation of μ-oxo-dimer.

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