Generation of Fe^{III}OEP–Hydrogen Peroxide Complex (OEP = octaethylporphyrinato) by Reduction of Fe^{II}OEP–O$_2$ with Ascorbic Acid Sodium Salt

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ESR and optical absorption spectra have been recorded for a frozen dimethylformamide (DMF) solution of the complex Fe^{III}OEP($^-$OH)($^-$OOH) (OEP = octaethylporphyrinato) prepared by mixing Fe^{II}OEP(pyridine)–O$_2$ with ascorbic acid sodium salt.

We have reported the formation of the Fe^{III}TPP–hydrogen peroxide adduct (TPP = tetraphenylporphyrinato),[1] demonstrated by simultaneous ESR and optical measurements carried out at 77 K.[2] Based on these observed results, the structure of the complex Fe^{III}TPP–hydrogen peroxide was assumed to be the six-co-ordinate Fe^{III}TPP($^-$OH)($^-$OOH) complex.[1] Here, we report the formation of the complex Fe^{III}OEP–$^-$OOH by reduction of Fe^{II}OEP–O$_2$ with ascorbic acid sodium salt (AscNa) in the presence of water.

The optical absorption spectrum recorded for the frozen dimethylformamide (DMF) solution of Fe^{II}OEP(pyridine)–O$_2$ (1.0 mM, 0.4 ml) showed absorption maxima at 536 and 568 nm [Figure 1(a)], which agreed well with that recorded at −45 °C.[3] On the other hand, the ESR spectrum of the same frozen solution was almost silent; a small amount of ferric high-spin species ($g_\perp$ = 6 and $g_\parallel$ = 2) was detected [Figure 2(a)]. Next an aqueous solution of AscNa (0.2 M, 0.02 ml) was added at −40 °C, and the mixture was immediately frozen to 77 K. As shown in Figure 2(b), the ESR spectrum revealed formation of the ferric low-spin complex [denoted as complex (**A**); g_1 2.286, g_2 2.171, and g_3 1.953] with the free radical species derived from AscNa (g 2.006). However, the optical spectrum of the same frozen solution showed a pair of new absorption maxima at 556 and 604 nm [Figure 1(b)]. The ESR

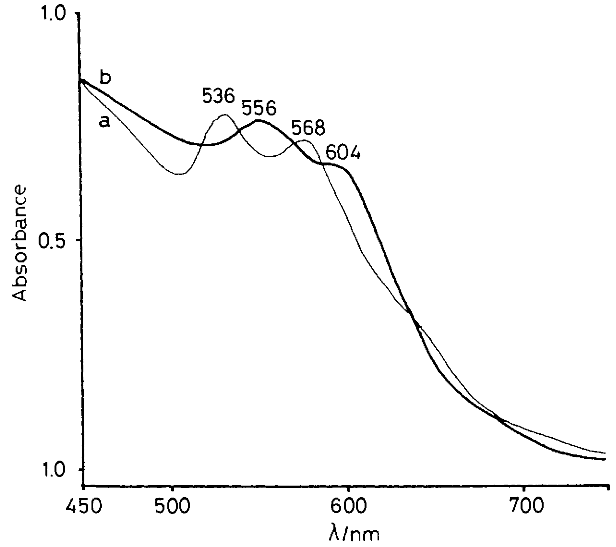


Figure 1. Optical absorption spectra recorded at 77 K: (a) Fe^{II}OEP(pyridine)–O$_2$ and (b) Fe^{III}OEP($^-$OH)($^-$OOH) (**A**) prepared by addition of aqueous AscNa to Fe^{II}OEP(pyridine)–O$_2$.

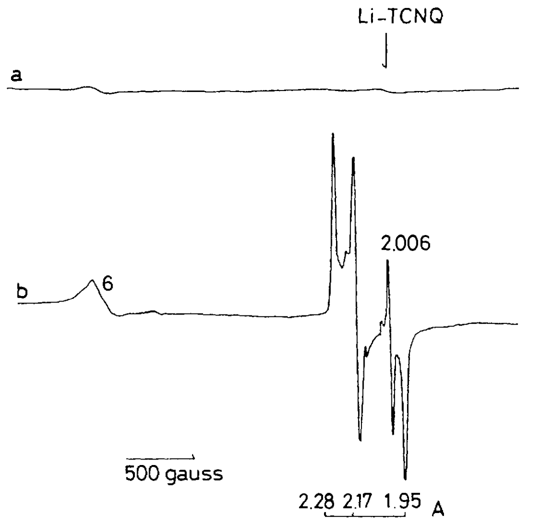
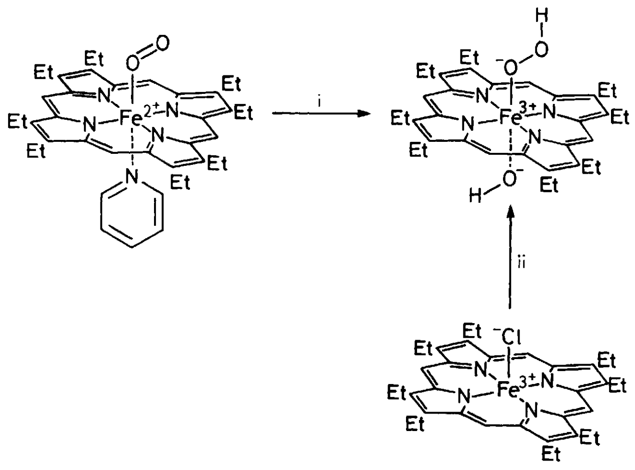


Figure 2. ESR spectra recorded at 77 K: (a) (TCNQ = tetracyanoquinodimethane) Fe^{II}OEP(pyridine)–O$_2$ and (b) Fe^{III}OEP($^-$OH)($^-$OOH) (**A**) prepared by addition of AscNa to Fe^{II}OEP(pyridine)–O$_2$.

Table 1. Optical and ESR properties of Fe^{III}OEP($^-$OH)($^-$OOH) and related complexes.

Complex	T^a/K	λ_{max}/nm			g_1	g_2	g_3	Ref.
Fe^{II}OEP(Py)O$_2$	77	405	536	568				[b]
	228	402	536	568				[b]
	228		530	563				3
Fe^{III}OEP($^-$OH)($^-$OOH)	77[c]		556	604	2.286	2.171	1.953	[b]
	77[d]		556	604	2.287	2.171	1.955	[b]
Fe^{III}TPP($^-$OH)($^-$OOH)	77		562	604	2.269	2.162	1.961	1

[a] Temperature for optical measurements. [b] This work. [c] Prepared by reduction of Fe^{II}OEP(Py)O$_2$ with AscNa. [d] Prepared by mixing Fe^{III}OEPCl and hydrogen peroxide.



Scheme 1. Probable mechanism of Fe^{III}OEP($^-$OH)($^-$OOH) complex formation: i, reduction of Fe^{II}OEP(pyridine)O_2 by AscNa in the presence of water ($^-$OH); ii, ligation of the $^-$OOH anion at the axial position of Fe^{III}OEPCl.

spectrum of the complex (**A**) was not observed on mixing Fe^{II}OEP–O_2 with an aqueous solution of ascorbic acid instead of AscNa, but was observed on addition of aqueous K_2CO_3 to the reaction mixture. This indicates that the complex (**A**) is generated by reduction of Fe^{II}OEP–O_2 with ascorbic acid under alkaline conditions. The same ferric low-spin complex was also recorded by mixing Fe^{III}OEPCl and aqueous hydrogen peroxide in the presence of KOH (Table 1).

As summarized in Table 1, the ESR and optical parameters of complex (**A**) agree well with those of the complex Fe^{III}TPP($^-$OH)($^-$OOH) (g_1 2.269, g_2 2.162, and g_3 1.961; $\lambda_{max.}$ 562 and 604 nm).[1] From comparison of the ESR and optical parameters of (**A**) and Fe^{III}TPP–hydrogen peroxide, (**A**) is assumed to be Fe^{III}OEP($^-$OH)($^-$OOH), in which the fifth co-ordination position of the Fe^{II}OEP(pyridine)O_2 complex is replaced by an $^-$OH anion from H_2O. As illustrated in Scheme 1, an identical complex Fe^{III}OEP($^-$OH)($^-$OOH) complex is generated by reduction of Fe^{II}OEP–O_2 with AscNa, or by mixing Fe^{III}OEPCl and hydrogen peroxide under alkaline conditions. These findings also demonstrate that atmospheric molecular oxygen (O_2) is activated to the peroxide anion ($^-$OOH) species reacting with the ferrous haem species (Fe^{II}OEP) and AscNa. The formation of the haem–OOH complex was assumed in the mono-oxygenation processes of cytochrome P-450,[4] and the P-450–hydrogen peroxide complex was thought to be produced by reduction of the P-450–oxygen complex with NADPH containing P-450 reductase.[4] However, the exact co-ordination and electronic structures are still equivocal at the submolecular level. The complex (**A**) will be a practical model for the intermediate haem–hydrogen peroxide complex of P-450.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

Received, 1st September 1989; Com. 9/03730F

References

1 K. Tajima, *Inorg. Chim. Acta*, 1989, **164**, 115.
2 K. Tajima, J. Jinno, K. Ishizu, H. Sakurai, and H. Ohya-Nishiguchi, *Inorg. Chem.*, 1989, **28**, 709.
3 C. H. Welbone, D. Dolphin, and B. R. James, *J. Am. Chem. Soc.*, 1981, **103**, 2869.
4 R. E. White and M. J. Coon, *Ann. Rev. Biochem.*, 1980, **49**, 315.