Stable Oxo-iron(IV) Porphyrin π Radical Cation Related to the Oxidation Cycles of Cytochrome P-450 and Peroxidase

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A porphyrin having twelve phenyl groups was synthesized and the stable oxo-iron(IV) porphyrin π radical cation at 8 °C was formed by the reaction of this porphyrin iron(III) complex and *m*-chloroperbenzoic acid.

One of most important problems in the oxidation cycles of cytochrome P-450 and peroxidase is the complete confirmation of the high valent iron porphyrin intermediate.[1] This intermediate is unstable at ambient temperature and only studies at low temperature have been performed.[2] Hence, we have attempted to prepare stable high valent iron porphyrin intermediates at ambient temperature. We report here the UV–VIS, ESR and NMR spectroscopic data of stable oxo-iron(IV) porphyrin π radical cations at 8 °C, which are prepared by the reaction of the new type of porphyrin iron complex with *m*-chloroperbenzoic acid.

The structure of the new porphyrin **1**, 5,10,15,20-tetrakis (2′,6′-dichlorophenyl)-2,3,7,8,12,13,17,18-octaphenylporphyrin, is shown in Fig. 1.[3] Porphyrin **1** is very soluble[3–5] and the UV–VIS spectrum in chloroform shows the broad Soret absorption at 460 nm, which differs from that (417 nm) of tetrakis(2,6-dichlorophenyl)porphyrin, which lacks the eight phenyl groups. The introduction of eight phenyl groups into the pyrrole moieties thus causes a red shift of 43 nm. The porphyrin **1** has weak fluorescence peaks at 715 and 775 nm.[3,6]† Porphyrin **1** was converted into the Fe^{III} complex by the iron(II) bromide–DMF (DMF = dimethylformamide) method[4,5] and the purity of this complex was confirmed by TLC. The visible spectrum of this complex in methylene chloride showed two strong peaks at 452 ($\varepsilon = 2.7 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$) and 396 nm.

In order to prepare the high valent iron porphyrin intermediate, the reaction of porphyrin **1** iron(III) chloride (1×10^{-5} mol dm^{-3}) with *m*-chloroperbenzoic acid (*m*-CPBA) (3×10^{-5} mol dm^{-3}) was performed in methylene chloride at 8 °C. The UV–VIS spectrum of the reaction mixture changed with time as shown in Fig. 2. After 10 minutes, broad peaks of weak intensity were observed (curve 2); *i.e.* two broad peaks at 443 and 380 nm, which were blue shifted from the original peaks (452 and 396 nm), were observed and a new broader peak from 720 to 820 nm appeared as shown in Fig. 2. The addition of cyclooctene (6×10^{-5} mol dm^{-3}) to this solution caused a distinct spectral change; the intensities of the two peaks at 443 and 380 nm increased with time, but the intensity of the new broader peak from 720 to 820 nm decreased with time (curve 3 and 4). Finally, the intensities and positions of the two peaks reverted to those of the original peaks (curve 1) as shown in Fig. 2. Gas chromatography analysis of this reaction solution showed the quantitative conversion from cyclooctene to cyclooctene oxide. This result means that the spectrum of curve 2 is due, not to a decomposed porphyrin **1** iron complex species, but to a new species which is formed by the reaction of porphyrin **1** iron(III) complex with *m*-CPBA. Groves *et al.* reported the formation of oxo-iron(IV)tetrakis(2,4,6-trimethylphenyl)porphyrin π radical cation at −42 °C and the UV–VIS spectrum of this intermediate is very similar to the spectrum of curve 2.[7]

In order to confirm the presence of this species, ESR measurements of this reaction were performed in toluene solution at 8 °C. Before addition of *m*-CPBA, the strong absorption ($g = 2.003$) of low spin Fe^{III} was observed. After addition of *m*-CPBA, the intensity of this absorption decreased with time and finally, ESR signals of Fe^{III} complex were absent. When cyclooctene was added to this solution, the intensity of absorption recovered with time. These ESR observations corroborate the UV–VIS measurements. It has already been reported that the *meta* proton peaks of tetrakis(2,6-dichlorophenyl)porphyrin Fe^{III} chloride in CD_2Cl_2 appeared at δ 12.8 and 14.1, and the *meta* proton peaks of this oxo-iron(IV) porphyrin π radical cation were observed at δ 38.9 and 38.0[8,9] Thus, the NMR spectra (270 MHz) of the new species arising from the reaction of porphyrin **1** iron(III) with *m*-CPBA were measured. The *meta* proton peaks of the 2′,6′-dichlorophenyl groups of porphyrin **1** iron(III) chloride complex in CD_2Cl_2 appeared at δ 13.2 and 13.7. After addition of *m*-CPBA solution, these peaks shifted to δ 41.6

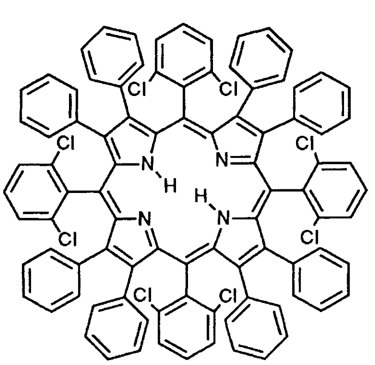

Fig. 1

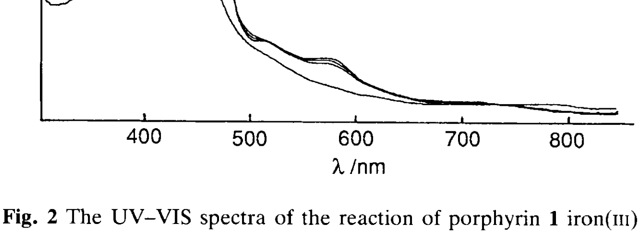

Fig. 2 The UV–VIS spectra of the reaction of porphyrin **1** iron(III) chloride with *m*-chloroperbenzoic acid (*m*-CPBA) at 8 °C. 1; porphyrin **1** Fe^{III} Cl^- (1×10^{-5} mol dm^{-3}) in CH_2Cl_2; 2; porphyrin **1** Fe^{III} Cl^- (1×10^{-5} mol dm^{-3}) in CH_2Cl_2 + *m*-CPBA (3×10^{-5} mol dm^{-3}) in CH_2Cl_2; 3 and 4; porphyrin **1** Fe^{III} Cl^- (1×10^{-5} mol dm^{-3}) in CH_2Cl_2 + *m*-CPBA (3×10^{-5} mol dm^{-3}) in CH_2Cl_2 + cyclooctene (6×10^{-5} mol dm^{-3}). The times after the addition of cyclooctene are 2 min (curve 3) and 6 min (curve 4), respectively.

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† Recently, Barkigia *et al.* reported the same observation in 5,10,15,20-tetrasphenyl-2,3,7,8,12,13,17,18-octaethylporphyrin.[6]

and 41.0. These values are close to those of oxo-iron(IV) π radical cation of tetrakis(2,6-dichlorophenyl)porphyrin.[9,10] Thus, the species giving curve 2 from the reaction of porphyrin **1** Fe^{III} chloride complex with *m*-CPBA may be assigned the oxo-iron(IV) porphyrin π radical cation [OFe^{IV} porphyrin$^{+\bullet}$]. When the same experiment was performed in methanol–methylene chloride (1 : 3), the reaction proceeded slowly and the UV–VIS spectrum of this intermediate was observed at 5 °C. This spectrum did not change for 10 h and, therefore, the oxo-iron(IV) porphyrin **1** π radical cation formed in this system is very stable. This is the first spectroscopic observation of a high valent iron porphyrin intermediate at ambient temperature and studies of the single crystal X-ray analysis of this complex are in progress.

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