THE REACTION OF THE SUPEROXIDE ION WITH IRON(III)PROTOPORPHYRIN IX DIMETHYL ESTER PERCHLORATE: EVIDENCE FOR A STABLE DIOXYGEN COMPLEX.

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SUMMARY: The reaction of superoxide ion with one equivalent of iron(III)protoporphyrin IX dimethyl ester perchlorate in NN-dimethylformamide at -50°C yields a complex with an absorption spectrum comparable to that of oxymyoglobin. The complex decomposes at -10° to iron(II)protoporphyrin IX dimethyl ester which does not react with oxygen.

The nature of the dioxygen complexes of myoglobin and hemoglobin continues to attract attention (1,2) particularly with regard to the role of the protein in stabilising the complexes. There have been numerous attempts (3-5) to reproduce some aspects of the chemistry of these biological systems in simpler iron complexes. As part of a continuing interest (6) in the chemistry of the superoxide ion, we have investigated its reactions with a number of metal complexes. Intrigued by the revival (7) of an earlier (8) proposal that the dioxygen complexes of the heme proteins could be formulated as superoxide derivatives of iron(III) (analgous to the extensively investigated (9) coboglobins), we chose to study the reaction of superoxide ion with a simple heme derivative, iron(III)protoporphyrin IX dimethyl ester perchlorate, $[Fe(III)(PPDE)]^{+}$ ClO_4^{-}, (I)

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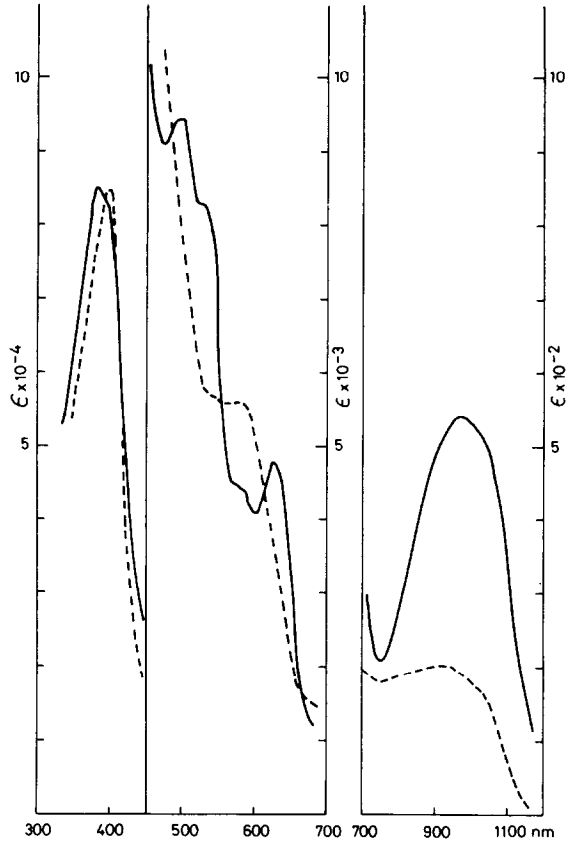

Fig.1. (a) Absorption spectrum of $[Fe(III)(PPDE)]^+ ClO_4^-$ in DMF at -50°C (————)

(b) Absorption spectrum of Fe(II)(PPDE) in DMF at -50°C(----)

RESULTS: The spectrum (Figure I(a)) of a solution of I in dry NN-dimethylformamide (DMF), is typical (10) of a high spin iron(III) heme. Such a solution reacts rapidly at -50°C with an electrochemically-prepared (11) solution of tetrabutylammonium superoxide,(II), in the same solvent. The spectrum of the product of this reaction is shown in Figure 2(a). This spectrum has many features similar to those of the various oxy-heme proteins, oxyhemoglobin, oxyperoxidase and is compared with that (2,12) of oxymyoglobin in Figure 2. The wave-lengths of the visible α- and β-bands and the u.v. Soret bands are

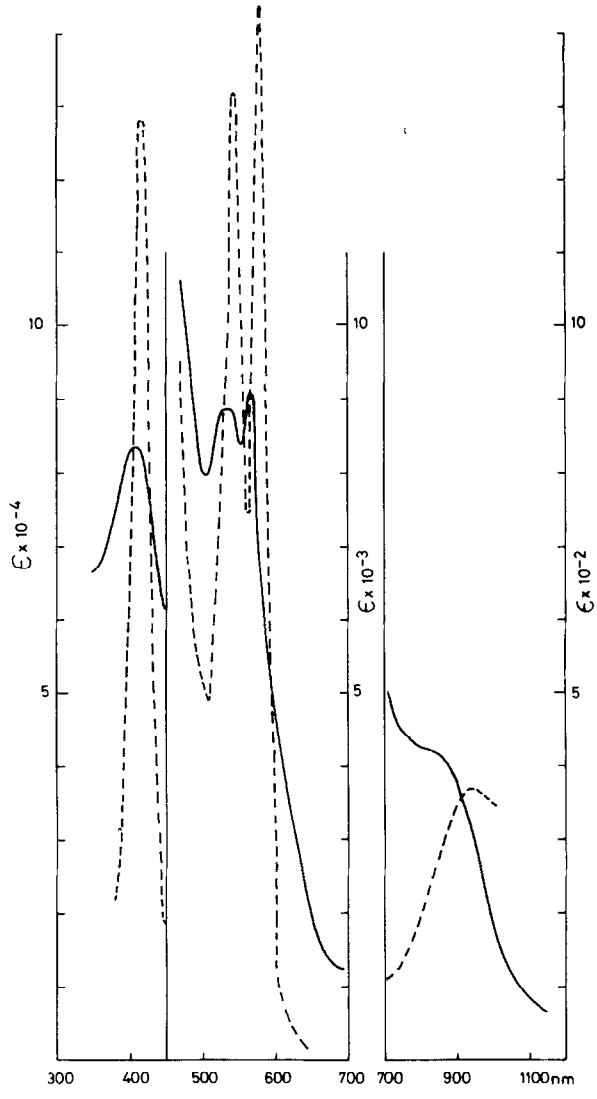

Fig.2. (a) Absorption spectrum of the product of the reaction between $[Fe(III)PPDE]^{+}ClO_4^{-}$ and tetrabutylammonium superoxide in DMF at -50°C, (———)

(b) Absorption spectrum (2,12) of oxymyoglobin in water pH 7 at 20°C, (----)

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similar; the α-band is more intense than the β-band and most importantly there is absorption in the infra-red in the form of a pronounced shoulder at 825 nm, compared to 950 nm in oxymyoglobin.

The absolute intensities of the α- and β-bands are lower than in oxymyoglobin though closer to oxyperoxidase (1). However since the bands of oxymyoglobin are narrower, the oscillator strengths of the bands may be comparable in the heme proteins and in the simple complex. Assuming that the product of the reaction is a dioxygen heme complex, the differences in line width and wavelengths of the absorption maxima (particularly the infra-red bands) may be due to different ligands <u>trans</u> to the oxygen and/or the different effective dielectric of the environment of the heme, The overall stoichiometry of the reaction is revealed in Figure 3 where an end-point is observed at a 1:1 ratio of I to II, again consistent with the product of the reaction being a dioxygen complex of iron protoporphyrin dimethyl ester:

$$[Fe(III)(PPDE)]^{+}ClO_4^{-} + Bu_4N^{+}O_2^{-} \rightarrow O_2Fe(PPDE) + Bu_4N^{+}ClO_4^{-} \qquad (1)$$

On warming a solution containing the product of the reaction between I and II, the spectrum changes to one identical to that of Fe(II)(PPDE) Figure 1(b), prepared by electrochemical reduction of I at -0.4V V^{S} S.C.E in DMF. Neither the product of the decomposition of the dioxygen

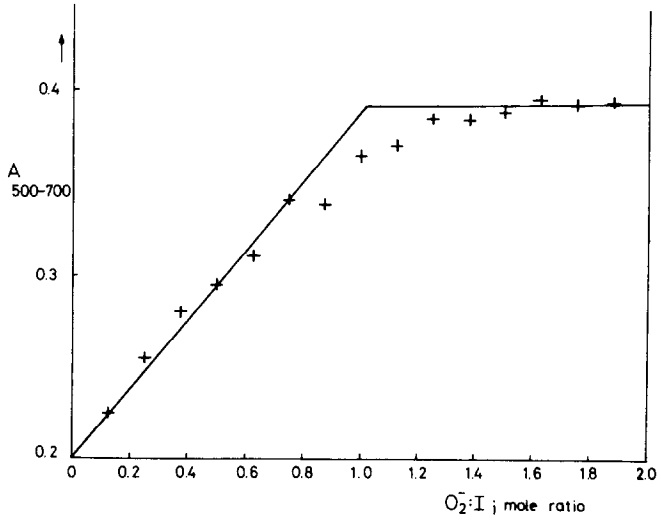

Fig.3. Titration of $[Fe(III)PPDE]^{+}$ ClO_4^{-} with tetrabutylammonium superoxide in DMF at -50°C.

complex nor Fe(II)(PPDE) react with molecular oxygen at temperatures from 25° to -50°C suggesting that overall reaction

$$O_2Fe(PPDE) \rightarrow O_2 + Fe(II)(PPDE) \qquad (2)$$

is not reversible.

The electron paramagnetic resonance spectrum of II (g_1 = 2.04; g_2 = 2.009; g_3 = 2.004, in DMF at -120°C) also serves as a convenient method of following the reaction since, irrespective of whether the product is formulated as a superoxide complex of iron(III) or a dioxygen complex of iron(II), a loss of intensity would be expected in that the former would be antiferromagnetically coupled and presumably the latter would be diamagnetic. On titration of a solution of II with I, the intensity of the e.p.r. spectrum of the superoxide diminishes and has vanished when one-equivalent of the porphyrin has been added.

DISCUSSION: The results suggest that the superoxide ion, being nucleophilic, can displace the solvent and the resulting complex with the iron porphyrin is stable with respect to decomposition at low temperature. Molecular oxygen, being a poor nucleophil cannot displace solvent from Fe(II)(PPDE) though presumably it must react with a five-coordinate iron(II) complex, the immediate product of the decomposition of the dioxygen complex. One of the functions of the protein in the heme proteins therefore may be to make available a five coordinate iron(II) complex. The method of preparation of the dioxygen complex described herein might be thought to lend support to the formulation of this and the presumably analogous complexes of the heme proteins as superoxide derivatives of iron(III). This need not necessarily be so since, for example, electron transfer from superoxide to iron(III) might precede formation of the complex. However it is at least suggestive. Efforts to isolate the presumed dioxygen complex continue.

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