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INTERMEDIACY OF HEMATOPORPHYRIN Mn(III) CATION RADICAL IN THE DECAY OF HEMATOPORPHYRIN Mn(IV) IN ACIDIC MEDIA

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Oxidation-reduction behavior of manganese porphyrin has been received attentions[1,2,3] in connection with photosynthesis where manganese is shown to play an important role in oxidative decomposition of water[4]. We recently reported[1] the complex pH-rate profile of hematoporphyrin-Mn(IV) (II) decay to Mn(III) complex (I) in aqueous solution in the pH range 1-10, where it was shown kinetically that oxidation-reduction potential of II was higher than water in neutral condition assuming the parallelism between the oxidation-reduction potential and the decay rate known as Conant rule[5] which was based on the similar relationship, i.e., increase of the decay rate and the oxidation potential of I with the decrease of pH, observed at pH > 9.9, where II was relatively stable. At pH > 6.3, the reaction of II to give I followed simple pseudo-1st order kinetics, and the two rate constants (decrease of II and increase of I) coinsided.

At pH < 6.3, however, descrepancies arose between the two values. In the acid region, the rate of decrease of II was independent of the concentration of II which showed the reaction was still pseudo-1st order in nature and considerably larger than the rate of increase of I. The observation suggests that another mechanism such as formation of intermediate as well as usual direct 1st- order reaction is operating in the acid region.(Scheme I). In fact, at pH 1.1 a transient peak (λ_{max} 440 nm) was observed by means of a rapid-scan spectrophotometer (RA-1300, made in Union Giken Co. Ltd.) as shown in Fig. 1. The most probable candidate for the short-lived intermediate is the cation

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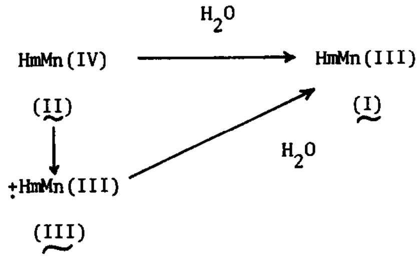

Scheme I

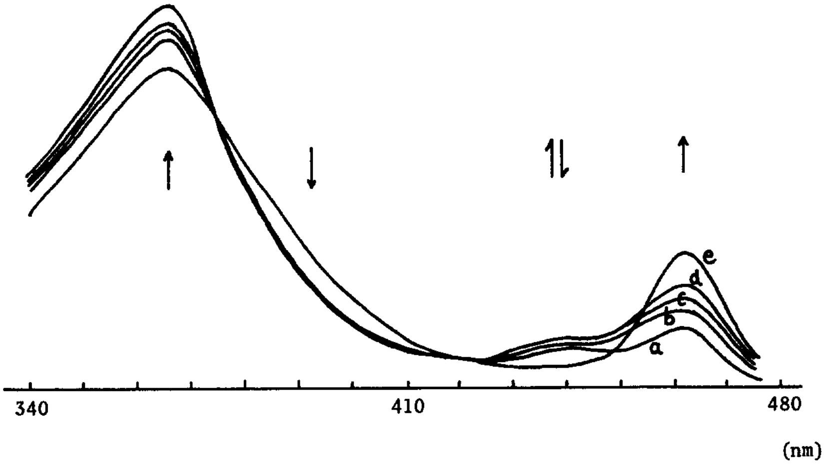

Fig 1. Rapid-scan spectrum of II to I at pH 1.1
Time Scale ; a:1, b:2, c:3, d:4 sec and e:infinite time

radical of I (III), which may arise from the electron transfer to Mn(IV) ion from the ligand, i.e., hematoporphyrin.

This assumption is also in accord with the following considerations. (i) High oxidation potential of II (at the pH investigated, more than 1 volt is predicted from the relationship between the decay rate and the potential), must exceed the oxidation potential of the ligand, because it was reported that ligand oxidation potentials of some M(II)tetraphenylporphyrins were ca. 1 volt at highest for several metals[6]. Since potential of similar order of magnitude should be expected for hematoporphyrin and the cation radical of

I (cation radical of the ligand) may be more stable than Mn(IV) hematoporphyrin in the low pH region, electron transfer $L\cdot Mn(IV) \longrightarrow L^{+\cdot}$ Mn(III) seems to be very reasonable. (ii) Detection of the similar short-lived intermediate (λ_{max} 440nm) on oxidation of I with Ce^{4+} was successful at pH 0.8 as shown in Fig 2. In this case, transient peak attributable to II was not detected. These facts are consistent with the above consideration in the sense that the lowest oxidation state of I is not metal-oxidized Mn(IV) state but ligand-oxidized cation radical III if the oxidation was carried out in *acidic* condition. Thus the assumption of intermediacy of the cation radical in L Mn(IV) decay after acidification is rationalized.

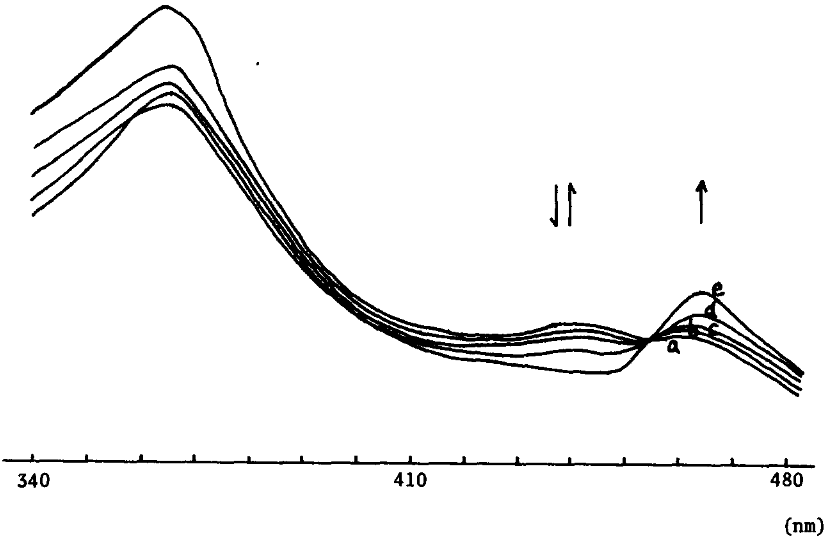

Fig. 2. Rapid-scan spectrum of the reaction of I with Ce^{4+} at pH 0.8
Time Scale ; a:0.2, b:0.6, c:1, d:2 sec and e:infinite time

Among the products of the reaction of II to give I at pH 2, water-soluble peroxide was detected. Thus after the reaction was over, I was extracted with chloroform and the aqueous layer was titrated iodometrically. Yield of total peroxide was 30 % based on Mn(IV) used. One of the peroxides obtained was hydrogen peroxide[7] which arose from the oxidation of water by II. This fact was in interesting contrast to the reported results at higher pH (10-13)[3] where the potential of **II** is much lower than that of water[2] and the product detected was side-chain oxidized peracid or diacyl peroxide of **I**[3].

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7. Formation of hydrogen peroxide was further evident on the basis of potentiometry with Ce^{4+}, where one of the product (7 % yield) showed the oxidation-reduction potential identical with that of hydrogen peroxide and the potential was exactly reproduced on addition of hydrogen peroxide after the titration was over.