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# COMPLEX pH-RATE PROFILE OF HEMATOPORPHYRIN-Mn(IV) DECAY

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Although little information is available about the environment of manganese in the *photosynthesis* where manganese is shown to be essential in oxidizing water to oxygen<sup>1)</sup>, the active species oxidizing water was assumed to be some porphyrin-Mn(IV) complex in neutral condition<sup>2)</sup>. The most convincing support for the assumption was that the oxidation-reduction potential, $E_{ox}$, of the hematoporphyrin-Mn(IV) complex (I) was observed to linearly increase with the decrease in pH in the pH range of 9.9-13.9. A simple extrapolation of the linear relationship leads to a conclusion that the $E_{ox}$ of I exceeds the $E_{ox}$ of water<sup>2)</sup> in magnitude. However, the measurements of the $E_{ox}$ of the Mn(IV) complex below pH 9.9 has never succeeded because of its extreme instability.

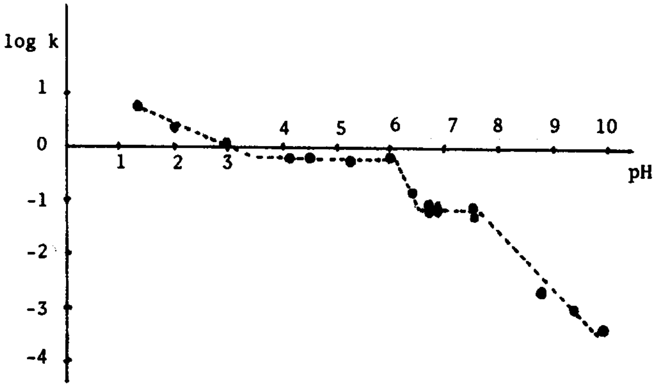

Figure 1. The pH-rate profile of the decay of I

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Now the authors wish to report that the pH dependence of the logarithmic decay of I was much more complex (see Fig. 1) than the linear relationship expected from the Calvin's assumption of the linear $E_{ox}$-pH relationship.

In the strongly alkaline solution, I, prepared from hematoporphyrin-Mn(III) complex (*II*) *and* NaOCl[2], *was very stable.* Thus the thermostated alkaline solution of *I* (pH *12* or 13) was quickly mixed with acid to adjust the final pH (pH range from 1 to 9) by use of a stopped flow apparatus and the decay was followed with a rapid-scan spectrophotometer.

The product was II independent of pH. It was concluded that the conversion from I to II was practically quantitative from the following observations; a) the final spectrum was identical with that of II independently prepared, b) the rate of the disappearance of I was equal to the rate of appearance of II except in acidic conditions (*vide infra*), c) clear isosbestic points were observed (at 375 ± 5 and 420 ± 5 nm) for a series of spectra at different times (see Fig. 2).

The complex pH-rate profile of the decay of I shown in Fig. 1 indicates that four species should exists for I, their populations being pH dependent. The difference in these species are most probably connected with the difference in the axial ligands which modify the $E_{ox}$ of I. A possible interpretation of the change in ligands is shown in Scheme 1 by considering their pKa.

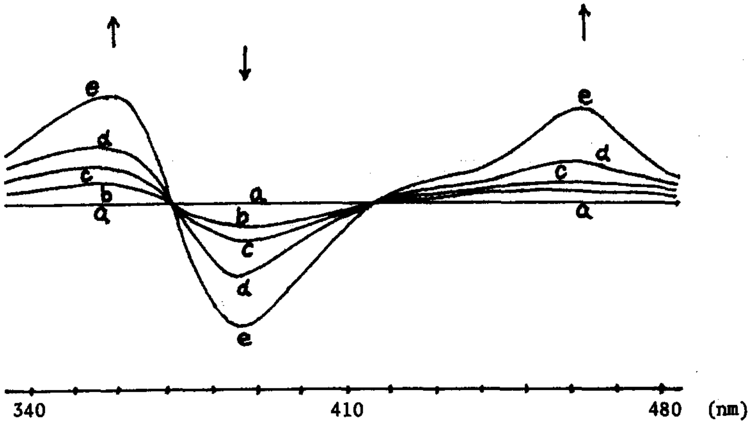


Figure 2. Difference spectrum of the decay of I at pH 2.95
a: 0.1 (reference), b: 0.2, c: 0.4, d: 1.0 sec, e: infinite time

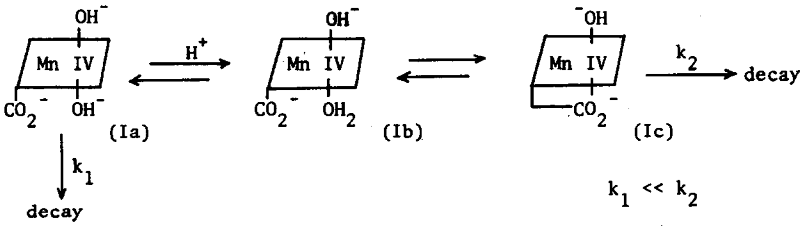
Table 1. Rate Constants[e] of the Reaction, [I] ⟶ [II]

| No. | acid or base added | pH | Decay of I, k, $sec^{-1}$ | Increase of II, k, $sec^{-1}$ | |
|---|---|---|---|---|---|
| 1 | $HNO_3$ | 1.35 | 6.40 ± 0.08 | 1.72 ± 0.04 | |
| 2 | $HNO_3$ | 2.03 | 2.12 ± 0.01 | 0.666 ± 0.010 | a |
| 3 | $HNO_3$ | 2.03 | 2.16 ± 0.04 | 0.655 ± 0.015 | b |
| 4 | $HNO_3$ | 2.00 | 2.52 ± 0.03 | 1.59 ± 0.02 | |
| 5 | $HNO_3$ | 2.95 | 1.18 ± 0.01 | 0.880 ± 0.012 | |
| 6 | $HNO_3$ | 4.10 | $(6.54 \pm 0.11) \times 10^{-1}$ | $(5.71 \pm 0.17) \times 10^{-1}$ | |
| 7 | $KH_2PO_4$ | 4.55 | $(7.67 \pm 0.31) \times 10^{-1}$ | $(4.81 \pm 0.11) \times 10^{-1}$ | |
| 8 | $KH_2PO_4$ | 5.25 | $(5.35 \pm 0.08) \times 10^{-1}$ | $(4.17 \pm 0.05) \times 10^{-1}$ | |
| 9 | $KH_2PO_4$ | 6.02 | $(6.73 \pm 0.16) \times 10^{-1}$ | $(4.73 \pm 0.07) \times 10^{-1}$ | |
| 10 | $HNO_3$ | 6.36 | $(1.43 \pm 0.02) \times 10^{-1}$ | $(1.46 \pm 0.03) \times 10^{-1}$ | |
| 11 | $KH_2PO_4$ | 6.72 | $(7.87 \pm 0.25) \times 10^{-2}$ | $(7.62 \pm 0.34) \times 10^{-2}$ | a |
| 12 | $KH_2PO_4$ | 6.72 | $(5.73 \pm 0.18) \times 10^{-2}$ | $(5.83 \pm 0.12) \times 10^{-2}$ | b |
| 13 | $KH_2PO_4$ | 6.83 | $(6.60 \pm 0.78) \times 10^{-2}$ | $(6.87 \pm 0.76) \times 10^{-2}$ | |
| 14 | $KH_2PO_4$ | 7.53 | $(5.43 \pm 0.02) \times 10^{-2}$ | $(5.78 \pm 0.18) \times 10^{-2}$ | c |
| 15 | $KH_2PO_4$ | 7.54 | $(7.32 \pm 0.26) \times 10^{-2}$ | $(6.08 \pm 0.24) \times 10^{-2}$ | d |
| 16 | $H_3BO_3$ | 8.75 | $(1.69 \pm 0.05) \times 10^{-3}$ | $(2.16 \pm 0.06) \times 10^{-3}$ | |
| 17 | $NaHCO_3$ | 9.30 | $(9.86 \pm 0.41) \times 10^{-4}$ | $(9.29 \pm 0.38) \times 10^{-4}$ | |
| 18 | $H_3BO_3$ | 9.87 | $(3.86 \pm 0.22) \times 10^{-4}$ | $(3.80 \pm 0.30) \times 10^{-4}$ | |

a. KCl $4.0 \times 10^{-4}$M was added. b. KCl $8.0 \times 10^{-4}$M was added. c. $[KH_2PO_4] = 0.012$ M.
d. $[KH_2PO_4] = 1.2$ M. e. mean value of ten runs.

Scheme 1 A Possible Interpretation of The Active Species

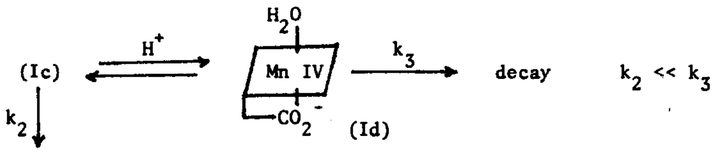
(a) pH > 7.6



(b) 6.4 ≤ pH ≤ 7.6

$$(Ic) \xrightarrow{k_2} decay$$

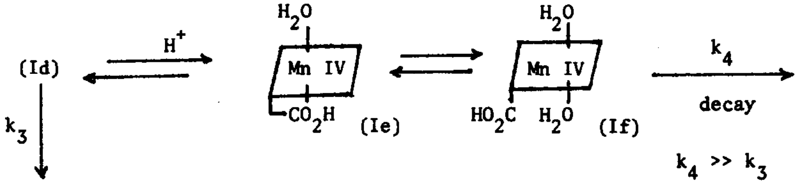
(c) $6.3 < pH < 6.4$



(d) $3.6 \leq pH \leq 6.3$

$$(Id) \xrightarrow{k_3} \text{decay}$$

(e) $pH < 3.6$



Effect of a buffer salt ( $KH_2PO_4$ ) on the rate was investigated in the concentration range from 0.012 to 1.2 M and was found not important (see Table 1). Appreciable but small effect of the chloride concentration on the rate was observed (Table 1), the effect was sufficiently small to exclude the important contribution of the oxidation of chloride (directly or as a bridging anion).

These small salt effects also excluded the possibility of the appreciable participation of any oxidizable impurity in these salts in the reduction of I.

Assuming the correlation between $E_{ox}$ and the rate of the oxidation-reduction reaction ( a kind of linear free energy relationship, known as Conant rule$^{3)}$), the present results indicate that Mn(IV) complexes such as I can effectively oxidize water at pH 9 or below$^{4)}$.

## REFERENCES

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4. In our preliminary experiments, the formation of some peroxide such as hydrogen peroxide, was observed in 30% yield in acid solution. The formation of oxygen has not yet been proved.