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# Mechanistic Studies on Oxidation Reaction of Ethane-Bridged Porphyrin Dimers to *trans*-Ethylene-Bridged Species

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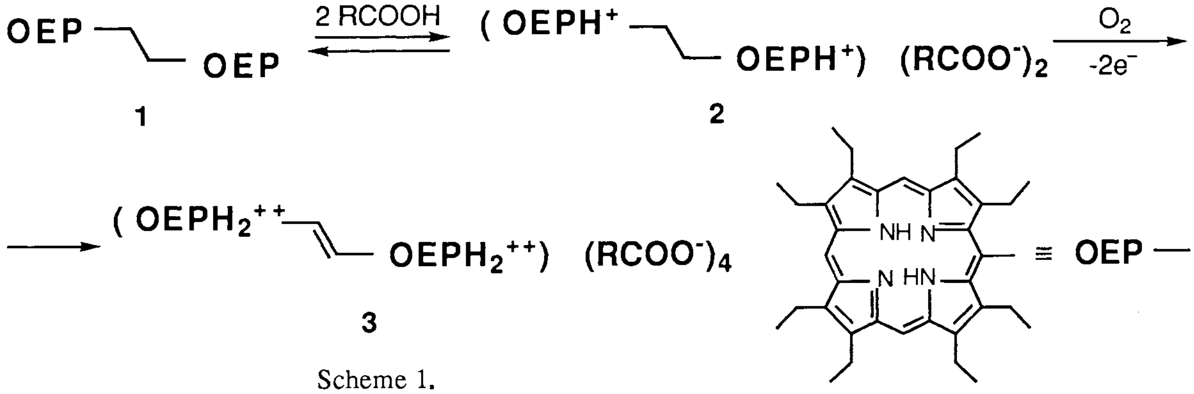
A facile aerobic oxidation of 1,2-bis(*meso*-octaethylporphyrinyl)ethane and other similar dimers to the corresponding *trans*-1,2-bis(*meso*-porphyrinyl)ethenes in several organic acids has been studied by UV-vis and $^1$H NMR spectroscopy and the general mechanism of the oxidation has been proposed. The key step of the oxidation is monoprotonation of the two porphyrin rings in dimer followed by two electron oxidation.

Recently rigid dimeric porphyrins with well-defined structural organization have attracted much attention as suitable photosynthetic models[1] as well as efficient catalysts for many biomimetic reactions.[2,3] We have developed convenient synthetic method[4,5] to prepare spatially fixed *trans*- and *cis*-ethylene bridged porphyrin dimers on the bases of acid catalyzed oxidation of the corresponding ethane-bridged dimer followed by *cis*-*trans* isomerization of the double bond. However, the mechanism of the novel oxidation reaction has not been revealed yet.



Scheme 1.

Here we report the mechanistic study of acid-catalyzed oxidation of 1,2-bis(*meso*-octaethylporphyrinyl)ethane (**1**)[4] (Scheme 1) and other ethane-bridged porphyrin dimers in oxygen saturated and unsaturated conditions.[6] The oxidation reaction of **1** was analyzed spectrophotometrically in seven different

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acids as shown in Table 1. The initial Soret band of **1** transformed gradually with time to the new Soret and visible absorption bands with an isosbestic point (Fig. 1). Therefore, the oxidation proceeds cleanly and the only **3** was detected during and after the reaction as will be discussed later. Pseudo-first-order rate constants ($k_{obs}$) were determined by a nonlinear least-squares fitting of the kinetic experimental data to the following equation

$$A_t = A_\infty + (A_0 - A_\infty)\cdot\exp(-k_{obs}t)$$

where $A_0$, $A_t$, and $A_\infty$ are absorbances of **3** at initial, intermediate, and final stages of the reaction, respectively and are summarized in Table 1.

It was found that only weak organic acids, which are able to protonate porphyrin structures to yield monocation species, promoted the oxidation reaction, while no products of oxidation were found in strong mineral or organic acids such as trifluoroacetic or formic acid which forms dication intermediates.$^{7)}$ The monoprotonation of both porphyrin rings in **1** seems to be a quite important factor, because no oxidation took place in mono- and dimetallated (Ni, Cu, Zn) complexes of **1** even in the weak acids. Therefore, it is concluded, as shown in Scheme 1, that the key step of the oxidation process is the formation of bis-monocation intermediate **2**. The elongation and/or branching of the acid alkyl chain considerably decreases $k_{obs}$ value presumably due to steric hindrance in formation of intermediate **2**.

It was assumed that the subsequent stage of the oxidation is carried out by oxygen. To prove this, the experiments were done under degassed conditions where there is no electron-transfer channel to oxygen, and only a complex mixture was obtained.$^{8)}$ A similar facile oxidation reaction by oxygen for the formation of

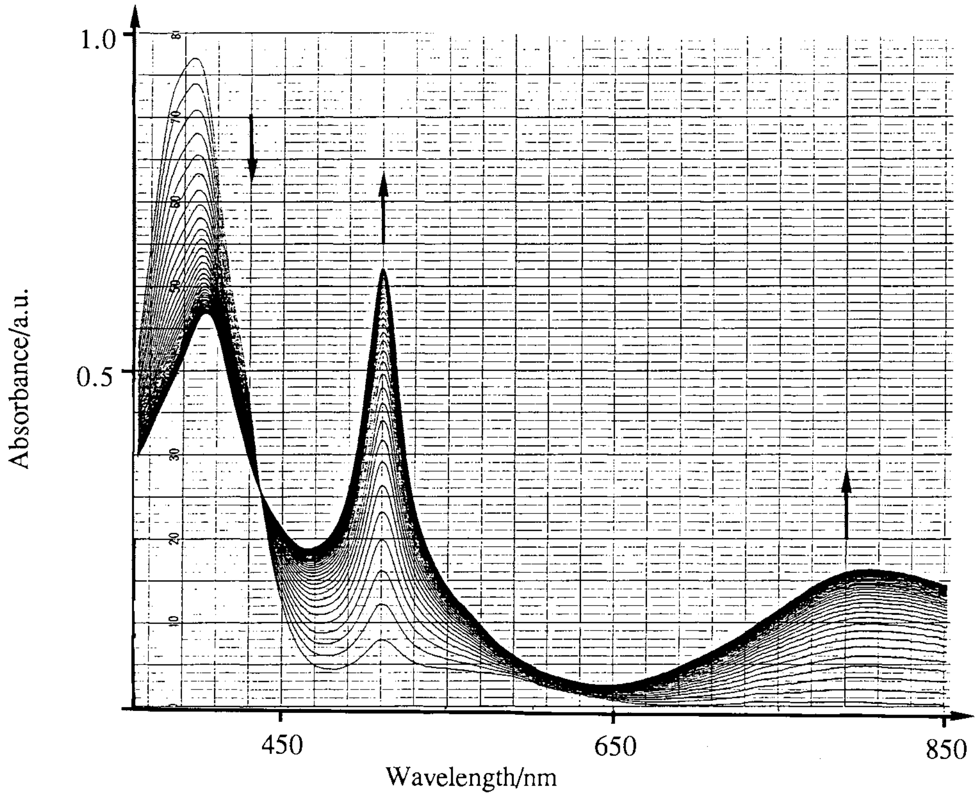

Fig. 1. UV-vis spectral changes of **1** in oxygen saturated $CH_3CH_2COOH$. Time interval between scans is 10 min.

diphenylacetylenes from stilbens has been reported.9) Two-electron transfer from intermediate **2** to oxygen and further protonation of porphyrin rings are expected to yield bis-dication dimer **3** (Scheme 1). The main active oxidant of this reaction seems to be triplet oxygen due to the following findings. First, the reaction proceeded with the same rate constant under light and dark conditions excluding singlet oxygen as active species. Secondly, small effect of radical scavengers ((*RS*)-α-tocopherol and 4-*t*-butylcatechol) (Table 2) and no detectable ESR signals during the reaction ruled out any long-lived radical intermediates in this reaction. (However, we can not exclude the existance of short-lived radicals formed by triplet oxygen.) The structure of **3** was supported by UV-vis and $^1$H NMR spectra which were the same as the spectra of *trans*-1,2-bis(*meso*-octaethylporphyrinyl)ethene (**4**) in corresponding acid indicating the dication species. Moreover, $^1$H NMR spectrum of **3** was similar to that of **4** in a mixture of $CDCl_3$/TFA-*d*4) which produces exclusively the dication species. Measurement of redox potentials revealed that reduction potential of **1** is more negative than that of **4**.10) Thus, the basicity of **4** is somewhat higher than that of **1** because under the same conditions **4** forms the dication while **1** produces only monocation.

Table 1. Absorption Data and Pseudo-First-Order Rate Constants For Acid Catalyzed Oxidation of Dimer **1**

| Acid | Relative ratio $I_{504-508}/I_{Soret}$ | $k_{obs}\cdot 10^{-3}$/ $min^{-1}$ a) |
|---|---|---|
| $CH_3COOH$ | 2.67 | 8.21 |
| $CH_3CH_2COOH$ | 1.51 | 6.21 |
| $CH_3(CH_2)_2COOH$ | 1.03 | 4.88 |
| $(CH_3)_2CHCOOH$ | 0.63 | 1.68 |
| $CH_3(CH_2)_3COOH$ | 0.68 | 1.74 |
| $CH_3(CH_2)_4COOH$ | 0.24 | 0.45 |
| $CH_3(CH_2)_5COOH$ | 0.23 | 0.31 |

a) Correlation coefficients were unity in all the measurements.

Absorption spectra of **3** in acid media showed "normal" Soret band at 401-406 nm and "florin" type absorption bands at 504-508 and 800 nm (Fig. 1). These spectra are similar to that of **4** in a mixture of $CHCl_3$/TFA and are distinguished from that of neutral free base.4) It might have resulted from the presence of equilibrium between bis-dication **3** and its tautomeric form in which the central double bond in **3** migrated to the adjacent position between *meso*- and *exo*-carbon atoms.11) This equilibrium is changed with changing the acid and shifted steadily to bis-dication form **3** from acetic to heptanoic acid with decrease in the ratio of intensities at 401-406 nm/504-508 nm from 1:2.67 to 1:0.23, correspondingly (Table 1).

Increase in the ionic strength of reaction media by addition of KSCN (2 mmol solution in EtCOOH) slightly accelerated the reaction by 1.1 times ($k_{obs} = 6.88 \times 10^{-3}$ $min^{-1}$), apparently due to the stabilization of the cationic species **2** and **3**. In AcOH unsaturated by oxygen the $k_{obs}$ value is also reduced by a factor of 2.2 ($k_{obs} = 3.68 \times 10^{-3}$ $min^{-1}$). The $k_{obs}$ value ($3.78 \times 10^{-3}$ $min^{-1}$) calculated on the basis of $^1$H NMR measurements in acetic acid-$d_4$ is similar to that calculated from UV-vis method.

For other porphyrin dimers with different alkyl substituents the similar oxidation reaction has been observed. It was found that oxidation rate constants are reduced with an increase of the steric hindrance of porphyrin substituents in the following sequence ($k_{obs} \times 10^{-3}/min^{-1}$ in AcOH): octaethyl- > ethio- (3.11) > copro- (2.51) > octapropylporphyrin (2.03). Such differences in the rate constants may be caused by difficulty in conformational changes of ethane-bridged dimers.12)

Thus, on the basis of spectral studies, the general mechanism for acid-catalyzed oxidation of ethane-bridged porphyrin dimers is proposed as involving the monoprotonation of the two porphyrin rings followed by the two electron transfer and further protonation of porphyrin rings. As far as our knowledge is concerned, this is the first example of facile aerobic oxidation promoted by monocation species of porphyrins.

Table 2. Effect of Radical Scavenger on Oxidation Reaction of **1**[a)]

| Scavenger | $k_{obs} \cdot 10^{-3}/min^{-1}$[b)]<br>1 mmol | 10 mmol | 100 mmol |
|---|---|---|---|
| (*RS*)-α-tocopherol | 5.33 | 5.20 | 5.04 |
| 4-*t*-butylcatechol | 5.32 | 5.39 | 3.80 |

a) Oxygen saturated conditions in $CH_3CH_2COOH$ (see Ref. 6).
b) Correlation coefficients were varied from 0.989 to 0.996.

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6) The oxidation procedure has been carried out in oxygen saturated acid solution (by oxygen bubbling during 20 min) and unsaturated condition (without oxygen bubbling) at 30 °C with $10^{-5}$ M concentration of ethane dimer **1** and monitored by UV-vis kinetic measurements with 10 ($CH_3COOH$, $CH_3CH_2COOH$), 30 ($CH_3(CH_2)_2COOH$, $(CH_3)_2CHCOOH$, $CH_3(CH_2)_3COOH$), and 60 min ($CH_3(CH_2)_4COOH$, $CH_3(CH_2)_5COOH$) intervals.

7) Formation of porphyrin monocation and dication species has been monitored by UV-vis spectroscopy. For review of spectral properties of mono- and dication porphyrin species see followed monopraph [illegible] M. Gouterman, "The Porphyrins," ed by D. Dolphin, Academic Press, New York - San Francisco - London (1978), Vol. III (Physical Chemistry, Part A), pp. 1 - 165; b) K. M. Smith, "Porphyrins and Metalloporphyrins," ed by K. M. Smith, Elsevier, Amsterdam - Oxford - New York (1975), pp. 1 - 58; c) Appendix, ibid, pp. 871 - 889.

8) In degased experiments the intermediate **2** is involved in rearrangement reactions due to delocalization of positive charge within porphyrin ring to produce other intermediates followed by decomposition of porphyrin structure after exposure to air.

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10) $E_{1/2}^{red}$ = -0.9 (**4**) and -1.38 V (**1**) measured by differential pulse voltammetry in 0.1 M tetrabutylammonium perchlorate solution of $CH_2Cl_2$ relatively to Ag/AgCl.

11) In spite of the "florin" type of UV-vis spectra of **3** no florin protons in $^1H$ NMR spectra have been found indicating that only migration of ethylene double bond to *meso*-position of porphyrin ring causes such unusual absorption for protonated porphyrins.

12) The existence of the two conformational forms of ethane-bridged dimers has been observed for sterically hindered coproporphyrin.

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