CHEMISTRY LETTERS, pp. 19 - 22, 1985.

THREE SPECIES OF PEROXOMOLYBDENUM PORPHYRINS FOUND IN THE REACTION OF OXO(5,10,15,20-TETRAKIS(4-N-METHYLPYRIDYL)PORPHINATO)-MOLYBDENUM(V) WITH HYDROGEN PEROXIDE

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The reaction of oxo(5,10,15,20-tetrakis(4-N-methylpyridyl)-porphinato)molybdenum(V) ($[Mo^{V}O(tmpyp)(OH_2)]^{5+}$) with H_2O_2 under different conditions produced three different species of peroxo-molybdenum complexes, i.e., $[Mo^{V}O(O_2)(tmpyp)]^{3+}$, $[Mo^{VI}(O_2)(tmpyp)(OH_2)]^{6+}$, and $[Mo^{VI}(O_2)_2(tmpyp)]^{4+}$.

In recent years dioxygen complexes of metalloporphyrins have been extensively studied because of their relevance to the biological oxygen transport, storage, and activating systems.1-5) Molybdenum(V) porphyrins are known to react with hydrogen peroxide in organic media to give diperoxomolybdenum(VI) porphyrins. The synthesis6) and photolysis7,8) of $Mo^{VI}(O_2)_2(tptp)$9) and electrochemistry10) of $Mo^{VI}(O_2)_2(tmtp)$9) have been reported. A different type of molybdenum porphyrin, $Mo^{V}O(O_2)(tpp)$,9) has also been studied.11) In this communication the formation of peroxomolybdenum(V) and -(VI) complexes of 5,10,15,20-tetrakis(4-N-methylpyridyl)-porphine in aqueous solution is described.

A water-soluble molybdenum(V) porphyrin complex, $[Mo^{V}O(tmpyp)(OH)]I_4$,9) was newly synthesized by methylating the four pyridyl groups of $Mo^{V}O(tpyp)(OH)$9) obtained by a modification of Murakami's method for the $Mo^{V}O(tpp)(OC_2H_5)$.12) The complex was identified by elemental analysis and IR spectroscopy. It is soluble over an entire pH range in aqueous solution. The acid dissociation of the axial water ligand in (monoaqua)oxo(5,10,15,20-tetrakis(4-N-methylpyridyl)porphinato)-molybdenum(V) ion, **1**, was studied spectrophotometrically. This hydrolysis is expressed as:

$$\underset{\mathbf{1}}{[Mo^{V}O(tmpyp)(OH_2)]^{5+}} \overset{K_a}{\rightleftharpoons} [Mo^{V}O(tmpyp)(OH)]^{4+} + H^+ \qquad (1)$$

pK_a was determined to be 7.18 ± 0.02 at 25 °C and I = 1.00 M ($NaNO_3$).13) The ESR spectrum of **1** in the acidic media at room temperature displays the typical feature for the molybdenum(V) porphyrin complexes previously reported,12,14,15) which consists of nine intense lines at the center and six weaker bands in a wider range. The g value of 1.969 is very close to those of $Mo^{V}O(tpp)X$ complexes in chloroform or dichloromethane (X: a monodentate ligand such as alkoxide or halide). The reaction of **1** with hydrogen peroxide in both acidic and neutral aqueous solutions was monitored by ESR and visible spectroscopy. Care was exercised to conduct the experiments in dark since the reaction is light-sensitive.

At pH 5-6 visible absorption spectra of the **1** solutions containing various amounts of H_2O_2 exhibit clear isosbestic points at 394, 469, and 529 nm (see Fig. 1). The conditional formation constant $K'_{Mo(V)}$ of the 1:1 peroxo complex was estimated at various hydrogen ion concentrations: $K'_{Mo(V)} = [1{:}1 \text{ complex}]\,[\mathbf{1}]^{-1}[H_2O_2]^{-1} = (3.7 \pm 0.5) \times 10\ M^{-1}$ at $[H^+] = 5.04 \times 10^{-6}$ M, $(1.15 \pm 0.05) \times 10^2\ M^{-1}$ at $[H^+] = 2.93 \times 10^{-6}$ M (see the inset in Fig. 1), and $(2.25 \pm 0.09) \times 10^2\ M^{-1}$ at $[H^+] = 2.06 \times 10^{-6}$ M. These values are consistent with the release of two protons in this peroxo complex formation. Thus the reaction of **1** with H_2O_2 at pH 5-6 can be expressed by Eq 2. The constant of equilibrium 2 was determined to be

$$\mathbf{1} + H_2O_2 \xrightleftharpoons{K_{Mo(V)}} \underset{\mathbf{2}}{[Mo^{V}O(O_2)(tmpyp)]^{3+}} + H_2O + 2H^+ \qquad (2)$$

$K_{Mo(V)} = [\mathbf{2}][H^+]^2[\mathbf{1}]^{-1}[H_2O_2]^{-1} = (9.6 \pm 0.7) \times 10^{-10}$ M at 25 °C and I = 1.00 M. The ESR spectrum of product **2** at room temperature is characteristic of the pentavalent molybdenum complex, though the superhyperfine structure cannot be observed under our experimental conditions as was the case for $[Mo^{V}(O_2)_2(tmtp)]^-$.10)

At pH lower than 3 the reaction is quite different: the intensity of ESR signals of **1** gradually decreases during the reaction with H_2O_2 and finally disappears. This indicates the formation of Mo(VI) (no d electron) species. The reaction is second order with respect to H_2O_2.16) In this process H_2O_2 plays two roles, namely as an agent oxidizing molybdenum(V) to molybdenum(VI) and as a ligand which displaces either an oxo group or a coordinated water molecule. The latter possibility can be excluded because the product still has a coordinated water molecule as mentioned later. These findings suggest the following reaction:

$$\mathbf{1} + 2H_2O_2 \longrightarrow \underset{\mathbf{3}}{[Mo^{VI}(O_2)(tmpyp)(OH_2)]^{6+}} + H_2O + OH^- + OH \qquad (3)$$

The free radical produced, OH, should be consumed by the fast reaction with H_2O_2 present in a large excess over the molybdenum complex.17)

When pH of the acidic solution of **3** thus obtained is raised with an NaOH solution in the presence of a large excess of H_2O_2, we observe the change of absorption spectra. Apparent molar absorption coefficients at 455 nm are plotted as a function of $-\log([H^+]/M)$ in Fig. 2. The solid line in Fig. 2 is calculated by the conditional formation constant, $K'_{Mo(VI)} = [\mathbf{4}][H^+]^2[\mathbf{3}]^{-1}$, where **4** is the product. Two protons are released in this reaction. Values of $K'_{Mo(VI)}$ at 25 °C and I = 1.00 M were obtained to be $(2.2 \pm 0.2) \times 10^{-9}\ M^2$ and $(4.8 \pm 0.4) \times 10^{-9}\ M^2$ at $[H_2O_2] = 0.295$ M and 0.739 M, respectively. The $K'_{Mo(VI)}$ values are nearly proportional to $[H_2O_2]$. Thus the reaction is considered to be written by eq 4.

$$\mathbf{3} + H_2O_2 \xrightleftharpoons{K_{Mo(VI)}} \underset{\mathbf{4}}{[Mo^{VI}(O_2)_2(tmpyp)]^{4+}} + H_2O + 2H^+ \qquad (4)$$

for which the equilibrium constant was obtained as $K_{Mo(VI)} = [\mathbf{4}][H^+]^2[\mathbf{3}]^{-1}[H_2O_2]^{-1} = (7.0 \pm 0.5) \times 10^{-9}$ M at 25 °C and I = 1.00 M. The consumption of one equivalent

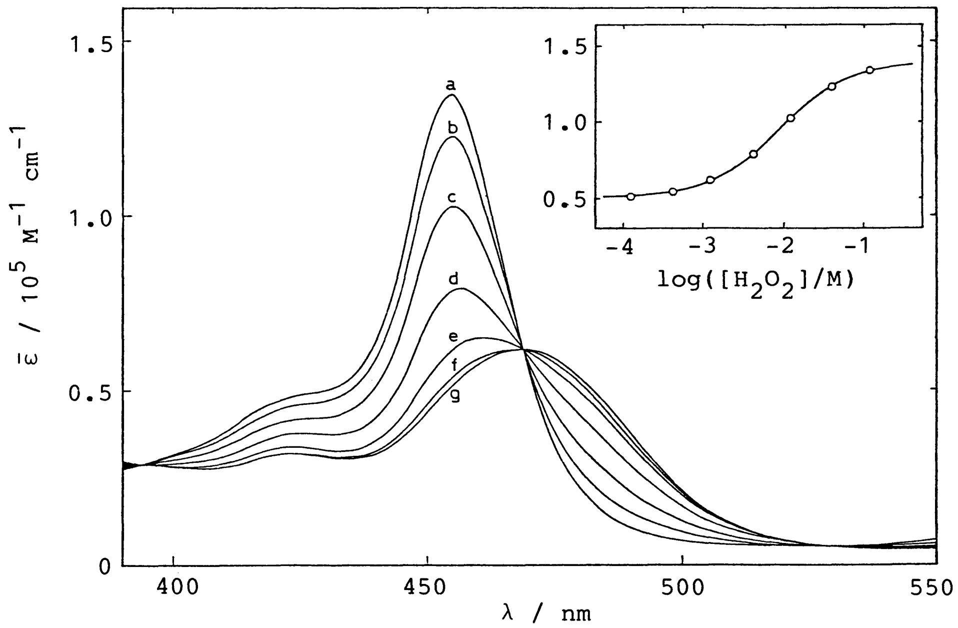

Fig. 1. Visible absorption spectra of the **1** solutions in the presence of various amount of H_2O_2. Experimental conditions are as follows: $C_{Mo(V)-TMPyP} = 1.04 \times 10^{-5}$ M, $[H^+] = 2.93 \times 10^{-6}$ M, I = 1.00 M, and 25 °C; total concentrations of H_2O_2 are 1.25×10^{-1} M (a), 4.16×10^{-2} M (b), 1.25×10^{-2} M (c), 4.16×10^{-3} M (d), 1.25×10^{-3} M (e), 4.16×10^{-4} M (f), and 1.25×10^{-4} M (g). (2-N-Morpholino)ethanesulfonic acid was used as a pH buffer agent. In the inset apparent molar absorption coefficients at 455 nm of each solution are plotted against -log([H_2O_2]/M). The curve was calculated by using the obtained values of the equilibrium constant and the molar absorption coefficient of **1** and **2**.

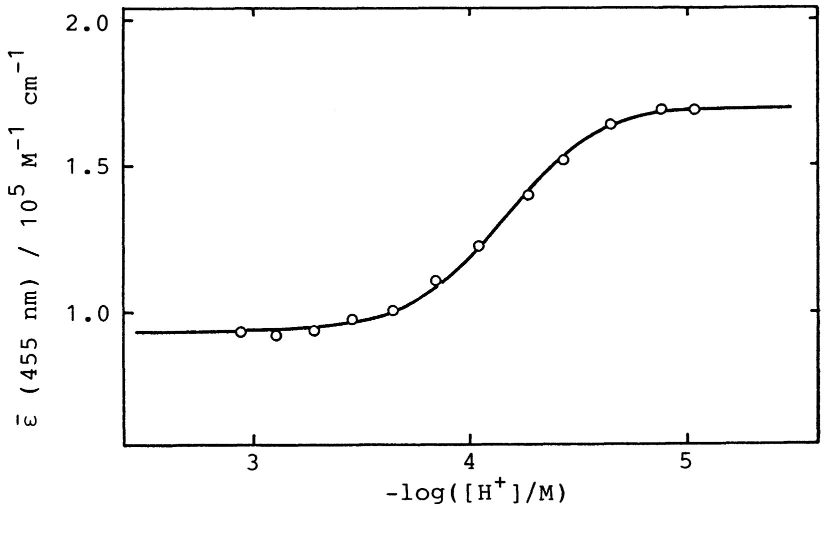

Fig. 2. Hydrogen ion concentration dependence of apparent molar absorption coefficients of the solution containing **3** and **4** in the presence of a large excess of H_2O_2 ([H_2O_2] = 0.295 M).

of H_2O_2 and the release of two protons in reaction 4 point to the substitution of a water molecule at the axial site of **3**. The diperoxo complex **4** seems to have a structure similar to that of $Mo^{VI}(O_2)_2$(tptp), which is obtained directly by the reaction of Mo^VO(tptp)(OH) with H_2O_2 in aprotic solvent.$^{6)}$

The authors thank Dr. Ryuichi Ikeda of Faculty of Science, Nagoya University for performing the ESR measurements. S. F. gratefully acknowledges financial support by a grant from the Kurata Foundation. Financial support from the Ministry of Education, Science, and Culture through a Grant-in-Aid for Scientific Research (No. 59430010) is gratefully acknowledged.

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9) Ligand abbreviations: H_2tptp, 5,10,15,20-tetra-p-tolylporphine; H_2tmtp, 5,10,15,20-tetra-m-tolylporphine; H_2tpp, 5,10,15,20-tetraphenylporphine; H_2tpyp, 5,10,15,20-tetra-4-pyridylporphine; H_2tmpyp, 5,10,15,20-tetrakis(4-N-methylpyridyl)porphine (TMPyP).
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(Received September 20, 1984)