Efficient Peroxide Decoloration of C.I. Acid Orange 7 Catalyzed by Manganese Mesoporphyrin Dimer Derivatives in Micellar Solutions

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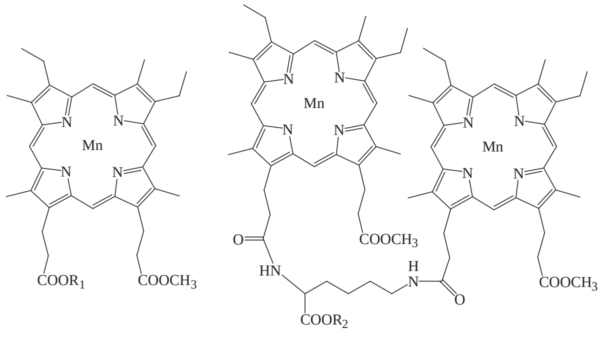
Manganese mesoporphyrin derivatives with hydrogen peroxide efficiently catalyzed the decoloration of C.I. Acid Orange 7 in micellar solutions under mild conditions such as pH 8.0 and 25 °C. The maximum peroxide oxidation rate was observed for histidine-linked manganese mesoporphyrin dimer in cetyltrimethylammonium bromide (CTAB) micelle.

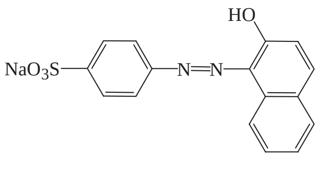
Porphyrin model compounds have been useful in providing insights into the reaction mechanisms of porphyrins in protein complexes, for example in key reactions found in oxidative electron-transfer systems such as peroxidases and cytochromes.[1–3] It is interesting to note that some peroxidases such as lignin-peroxidase, manganese peroxidase, and horseradish peroxidase catalyze the decoloration of azo dyes. Peroxidases are able to be used as bleaching agents, being not only more active than those currently available but also environmentally safer.[4–6] However, no reports have yet noted the catalytic effect of porphyrin upon the peroxidative decoloration of azo dyes in micellar solutions.



		R_1	R_2
1	MnMPDME	CH_3	—
2	MnMPMME-L-His-OMe	L-His-OMe	—
3	MnMP-L-Lys(MnMP)-OMe	—	CH_3
4	MnMP-L-Lys(MnMP)-L-His-OMe	—	L-His-OMe

Scheme 1. Manganese mesoporphyrin derivatives

C.I. Acid Orange 7



Scheme 2. Azo Dye

We now report biomimetic peroxidative-oxidation of azo dye (Scheme 2) catalyzed by mesoporphyrin derivatives (Scheme 1) in various surfactants, CTAB, sodium dodecyl sulfate (SDS), and Triton X-100, solutions with hydrogen peroxide under mild conditions such as pH 8.0 and 25 °C. The decoloration rate was depended on surfactant concentration, where the maximum decoloration rate was observed at the critical micelle concentration. This is the first report that manganese porphyrin catalyzed peroxidative decoloration in micellar solutions. The key to peroxidative decoloration is its usefulness in providing an insight into the catalytic effect of porphyrin structures on the decoloration in various micellar solutions. Manganese mesoporphyrins were selected because of their usefulness and solubility in micellar solutions.[3]

Manganese complexes of mesoporphyrins, **1**–**4** were prepared as described in the previous paper.[7] Characterization and verification of the compounds (Scheme 1), and the free base derivatives that had been synthesized, were performed by means of the following spectroscopic techniques; UV–vis. absorption spectroscopy, ^1H NMR, and MALDI-TOF-MS.[8] The visible spectra of the compounds in 10% EtOH–CH_2Cl_2 exhibited characteristic Mn(III) mesoporphyrins peaks[9] as described in previous papers.[3] The Soret band of Mn mesoporphyrins was shifted by 2 nm owing to the presence of a histidine residue on the compounds, indicating coordination between Mn atom of mesoporphyrin derivatives and N atom of imidazole residue.[7]

The effect of surfactants on the decoloration rate of the dye has been examined at pH 8.0 to provide an insight into the charge effect of the dye–surfactant interaction. Figure 1 shows that semilogarithmic plots of C_0/C_t against decoloration time gave a straight line passing through the origin for C.I. Acid Orange 7 in the presence of **1** in various micellar solutions. C_0 and C_t are the dye concentrations in the initial solution and at time t in Figure 1. Similar straight lines were observed for all cases, in which the increased line was observed because of the presence of Mn mesoporphyrin derivatives in micellar solutions. Enhanced decoloration of the dye was observed with the CTAB micelle. The decoloration rates were first order with respect to the dye concentration for the times. Eq 1 gives numerical values that can be used later to compare the compounds:

$$ln(C_0/C_t) = k_{\text{obs}}t \qquad (1)$$

The rate constant k_{obs} based on first-order kinetics is given in units of min^{-1} and summarized in Table 1. As is apparent from Table 1, the decoloration rate increased in the order, CTAB > Triton X-100 > SDS. Interestingly, an extremely enhanced decoloration by Mn mesoporphyrins with hydrogen peroxide

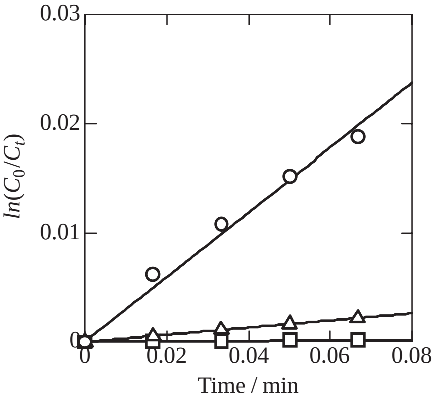


Figure 1. Plots of (C_0/C_t) against decoloration time for C.I. Acid Orange 7 catalyzed by **1** in various micellar solutions at 25 °C, pH 8.0. ([C.I. Acid Orange 7] $= 1 \times 10^{-4}$ M, $[H_2O_2] = 3 \times 10^{-2}$ M, **1** $= 1 \times 10^{-5}$ M, CTAB $= 1 \times 10^{-3}$ M, [Triton X-100] $= 2.5 \times 10^{-4}$ M, [SDS] $= 8 \times 10^{-3}$ M): CTAB (circles), Triton X-100 (triangles), and SDS (squares).

Table 1. Rate constants for decoloration of C.I. Acid Orange 7 catalyzed by manganese porphyrin derivatives

Catalyst	System	$k_{\mathrm{obs}}/\times 10^2\ \mathrm{min}^{-1}$
1	SDS	0.247
1	Triton X-100	2.79
1	CTAB	27.9
2	CTAB	215
3	CTAB	165
4	CTAB	389

[C.I. Acid Orange 7] $= 1 \times 10^{-4}$ M, $[H_2O_2] = 3 \times 10^{-2}$ M, **1** and **2** $= 1 \times 10^{-5}$ M, **3** and **4** $= 5 \times 10^{-6}$ M, [CTAB] $= 1 \times 10^{-3}$ M, [Triton X-100] $= 2.5 \times 10^{-4}$ M, [SDS] $= 8 \times 10^{-3}$ M.

was observed when CTAB was present.[10] The environment provided by CTAB micelles could be important for promoting complex formation between Mn mesoporphyrins and azo dyes, which results in oxidization. In contrast, the decoloration rate decreased strongly with increasing concentration of sodium chloride (data not shown). These results indicate that the decoloration rates depend on the surface of micellar structure, consistent with the result described previously.[11] It is likely that the complex formed between the azo dye and Mn mesoporphyrins with hydrogen peroxide in the micellar domain plays an important role in the decoloration rate.

Furthermore, as is apparent from Table 1, the decoloration rates increase in the order, **1** < **3** < **2** < **4**, indicating that the rate is largely dependent on the structures of Mn mesoporphyrins. The largest rate was observed in the presence of **4**. Comparing the decoloration rate and the structures of these Mn mesoporphyrins enables the following conclusion to be drawn. Coordination between Mn atom in the porphyrin ring and imidazole group in these Mn mesoporphyrin plays an important role on enhancement of the rate. This coordination determines the red shift of the Soret band of Mn mesoporphyrins as described elsewhere[7] and the imidazole moiety can more effectively enhance the decoloration as described previously.[12,13] Interestingly, the dimer derivatives enhance the decoloration much more effectively than the corresponding monomer derivatives. The precise mechanism for peroxide decoloration of dyes with hydrogen peroxide is not fully understood but is thought to be due to hydroxyl radicals reacting with the organic coloring agent and destroying the chromophore.[3,4] For example, after decomposition of C.I. Acid Orange 7 dye decoloration products present were 4-sulfophenyldiazene, 4-nitrosobenzene sulfonic acid, and quinone intermediates.[3,5] Electron paramagnetic resonance spectroscopy (EPR) measurement indicated the presence of Mn(IV)–Mn(III) oxo hybrid species in egg PC lipid bilayers at 5 K especially for **2** where 16-line EPR spectrum could be easily detected although not well observed for **1**.[14] This result implied that the imidazole moiety plays an important role in the evolution of Mn(IV)–Mn(III) oxo hybrid species where **2** can easily form this dimer complex with a resultant enhance decoloration rate compared with **1** and thus, dimer derivatives enhance the decoloration. However, further investigation will be necessary to determine the various roles indicated in oxidations by H_2O_2 catalyzed by Mn mesoporphyrin derivatives.

In conclusion, **2**, **3**, and **4** (Scheme 1) were synthesized. Mn mesoporphyrin derivatives with H_2O_2 in the presence of imidazole catalyze efficiently the peroxide oxidation of azo dyes in CTAB micellar solution under mild conditions such as pH 8.0 and 25 °C. The oxidation largely depends upon the structure of the mesoporphyrin derivatives and the presence of an imidazole moiety, whereupon the maximum decoloration rate of C.I. Acid Orange 7 was observed for **4**.

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9 UV–vis. spectra (10% EtOH–CH_2Cl_2). **1**: $\lambda_{\max}$ 458, 545 nm, **2**: $\lambda_{\max}$ 461, 548 nm, **3**: $\lambda_{\max}$ 459, 550 nm, **4**: $\lambda_{\max}$ 460, 550 nm.
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