

Structural Studies of Water-Soluble β -Brominated Manganese Porphyrins: Stabilities of MnTDCSPPBr₈ and MnTSPPBr₈ as Homogeneous and Supported Reagents Toward Hydrogen Peroxide and Sodium Hypochlorite

Hayrettin TÜRK, Hüseyin BERBER

*Anadolu University, Faculty of Sciences, Department of Chemistry,
26470 Eskişehir-TURKEY*

Received 27.03.2000

This article describes the structural stabilities of [2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinato]manganese(III) X (where X = H₂O and/or OH⁻, depending on pH) (MnTDCSPPBr₈) and [2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra(4-sulfonatophenyl)porphinato]manganese(III) X (where X = H₂O and/or OH⁻, depending on pH) (MnTSPPBr₈) toward H₂O₂ and NaOCl at various pH's, I = 0.2 M and 30°C. In addition, the structural stabilities of these manganese porphyrins were investigated when they were bound to quaternary ammonium containing supports, namely, hexadecyltrimethylammonium bromide (CTAB), 2,6-ionene, 2,10-ionene and a poly[(vinylbenzyl)trimethylammonium chloride] latex. In alkaline media, both manganese porphyrins degraded and precipitated even in the absence of both of the oxidants. In neutral and acidic solutions, they showed increasing stabilities toward H₂O₂ as pH decreased and almost no stabilities toward NaOCl. When bound to CTAB and the latex, they gained very high stabilities toward H₂O₂ at pH < 2 and almost no degradation was observed. On the other hand, the stabilities of the ionene-bound manganese porphyrins were close to the free complexes. The pseudo-first order degradation rate constants of MnTDCSPPBr₈, MnTSPPBr₈ and their supported analogues were determined.

Introduction

Metalloporphyrins show structural resemblance to cytochrome P-450, a class of enzymes that mediate a wide variety of oxygenations and the oxidative metabolism of exogenous compounds¹. Since the 1980's, in attempts to mimic the activity of cytochrome P-450, a large class of substituted metalloporphyrins have been synthesized and used as catalysts in oxidation of alkanes and alkenes²⁻⁸.

The driving force behind the advances made in porphyrin synthesis during the past ten to fifteen years was to prepare suitable porphyrins that are sufficiently stable toward oxidative degradation by strong oxidants and still catalytically active in the oxidation reactions. The stability of a porphyrin

depends on the nature of oxidizing species as well as on the substituents on the phenyl and pyrrole moieties of the porphyrins. A survey of the literature revealed that there are some studies which briefly deal with the stabilities of porphyrins toward oxidants under various conditions^{9–17}. In general, electron-withdrawing and bulky substituents, especially in the ortho positions of the phenyl groups, enhance the stability of porphyrins^{10–12,14,18–20}. That is why 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin, 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, 5,10,15,20-tetramesitylporphyrin are the chosen ligands of which the manganese and iron containing derivatives are commonly used as oxidation catalysts. These porphyrins containing substituents in their *meso*-aryl groups are called the second-generation porphyrins by Meunier⁶ and ‘type A’ porphyrins by Wijesekera et al.⁷ After a convenient synthesis of the second-generation porphyrins developed by Lindsey and co-workers^{21–23}, several research groups have taken the further step of preparing porphyrins with halogens substituted at the β -pyrrole positions. These highly substituted porphyrins are called the third-generation porphyrins or ‘type B’ or ‘type C’ porphyrins depending on the presence of substituents in the *meso*-aryl groups^{6,7}. Although it has been reported that electron-withdrawing substituents such as bromine at the β -pyrrole carbons had a profound influence on the redox potentials and caused distortion of the porphyrins from a flat conformation to a saddle-shaped conformation^{24,25}, it is not clear whether the third-generation porphyrins are more stable toward oxidative degradation than the second-generation ones under similar conditions. Banfi et al. reported that the halogenation of β -pyrrole carbons of some tetraarylporphyrins caused a decrease in their catalytic reactivity and robustness¹⁵. On the other hand, Meunier and co-workers found that manganese tetramesitylporphyrins containing halogen atoms at the β -pyrrole carbons were better catalysts than the unsubstituted ones^{19,20}. Usually it is implied that the halogenation of the β -pyrrole carbons should lead to more stable porphyrins.

In the metalloporphyrin-catalyzed reactions reported in the literature, oxidants have usually been used in equal or slightly higher amounts with respect to the metalloporphyrins, which have been used in very low amounts with respect to substrates. Under these conditions, the metalloporphyrins were protected by a large excess of substrate present in the reaction mixture and the yields of the oxidation reactions were usually based on the amount of oxidant consumed by the reaction instead of the amount of the oxidized substrate. In addition, the reactions employing water-insoluble metalloporphyrins as catalysts usually need to be carried out in a two-phase system where the water-soluble oxidants, which are responsible for degradation, are partitioned in the organic phase at a concentration that is much lower than that in the aqueous phase. In the two-phase systems, the stabilities of the metalloporphyrins may appear to be quite high despite the fact that a large excess of water-soluble oxidant is employed in the reactions. These reaction conditions may be misleading in connection with both the catalytic activities and the stabilities of the metalloporphyrins.

This study has been carried out to give insight into the structural factors governing the stabilities of MnTDCSPPBr₈ and MnTSPBr₈ when NaOCl or H₂O₂ is employed as oxidant. According to Wijesekera et al.⁷, MnTDCSPPBr₈ is a ‘C type’ metalloporphyrin whereas MnTSPBr₈ is a ‘B type’ one. By choosing these water-soluble manganese porphyrins instead of their water-insoluble analogues, we avoided using a two-phase system and a phase transfer catalyst which may influence their structural stabilities. Also, we did not add any substrate or ligating compound to the reaction mixture, which may cause change in the porphyrin stabilities as well. In addition, we were interested in finding the influence of the supports - 2,6-ionene, 2,10-ionene, hexadecyltrimethylammonium bromide (CTAB) and a quaternary ammonium group containing latex, on the structural stability of the manganese porphyrins attached to them.

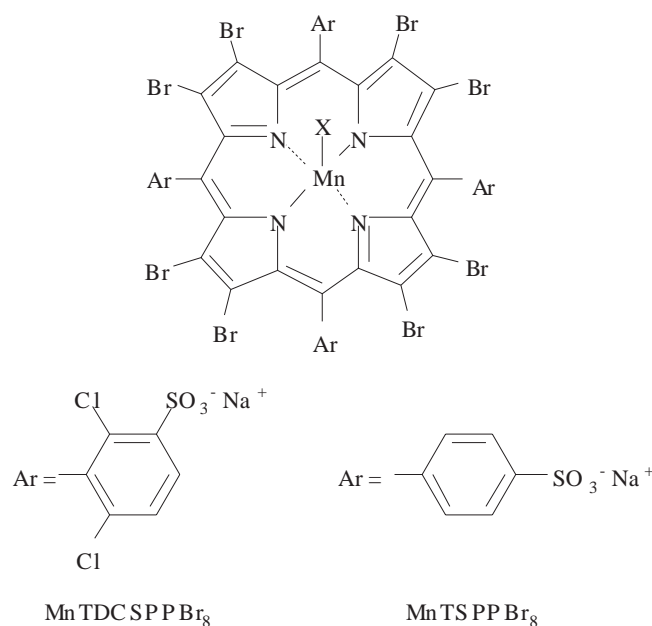
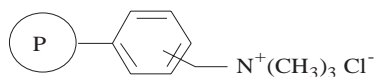
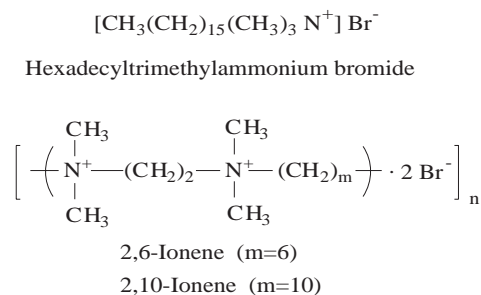


Figure 1. Structural formula of the manganese porphyrins.



Poly(vinylbenzyltrimethylammonium chloride) latex

Figure 2. Structural formula of the supports.

Experimental

Materials and Instrumentation

All chemicals purchased from Aldrich, Merck or Fluka were of reagent grade. The solvents used were fractionally distilled before use. 5,10,15,20-Tetraphenylporphyrin was prepared and purified according to the method of Adler et al.²⁶ and its β -bromination was carried out by the methods of Bhyrappa et al.⁵ and D'Souza et al.²⁷. Sulfonation of the β -brominated tetraphenylporphyrin (H_2TPPBr_8) was performed with H_2SO_4 (96%) at 100°C for 8 h. The manganese complex of the sulfonated product (H_2TSPBr_8) was obtained by the reaction with MnCl_2 in water at pH 7.0-7.5 at 75°C for 32 h. 5,10,15,20-Tetrakis(2,6-dichlorophenylporphyrin) (P_2TDCPP) was synthesized by the method of Lindsey et al.²¹⁻²³ The bromination of the β -positions of

H₂TDCPP was carried out with N-bromosuccinimide as described for the β -bromination of tetramesitylporphyrin by Hoffmann et al.^{19,28}. Sulfonation of the β -brominated tetraarylporphyrin (H₂TDCPPBr₈) was performed with H₂SO₄ (96%) at 120°C for 27 h. The manganese complex of the sulfonated product (H₂TDCSPPBr₈) was prepared in water by the reaction with MnCl₂ at pH 7.0-7.5 at 95°C for 40 h.

2,6-Ionene and 2,10-ionene were synthesized according to van Streun et al. with slight modifications²⁹. The numbers of average molecular weights (M_n) of these polyelectrolytes were determined to be 2700 and 4900, respectively, and determined by titration with sodium hydroxide after their amine-terminated end groups were converted to quaternary ammonium groups with hydrochloric acid²⁹. These M_n s correspond to 14.4 and 23.0 quaternary ammonium groups per molecule, respectively.

Poly[(vinylbenzyl)trimethylammonium chloride] latex was prepared in a previous study³⁰. It was 5% crosslinked and contained 3.58×10^{-3} mol quaternary ammonium groups per gram. The average particle size of the latex determined from TEM micrographs was 66 ± 16 nm.

UV-visible spectra were recorded on a Shimadzu UV-2101 PC spectrophotometer equipped with water-circulated thermostatted cell holders and obtained using 0.1 cm path-length spectrometer cells at 30°C. The samples were handled in air and daylight during the preparation and throughout the study.

General Procedure for Determination of Structural Stabilities of MnTDCSPPBr₈ and MnTSPBr₈

The changes in absorption spectra of the manganese porphyrins in the presence of either NaOCl or H₂O₂ at pH 1-9 were observed and the decrease in the absorbance of the Soret bands at λ_{\max} was used to calculate the degradation rates constants. The procedure was similar to the one employed for the determination of the stabilities of non β -brominated analogues of these manganese porphyrins, which is described elsewhere³¹.

Results and Discussion

The Structural Stabilities of MnTDCSPPBr₈ and MnTSPBr₈

The structural stabilities of the homogeneous MnTDCSPPBr₈ and MnTSPBr₈ and their supported analogues toward NaOCl and H₂O₂ were investigated at pH 1-9, I = 0.2 M and 30°C. Their degradation rate constants were also determined. These oxidants are commonly used as an oxygen source in the metalloporphyrin-catalyzed oxidations and hydroxylations. In the experiments, we employed high NaOCl and H₂O₂ concentrations relative to those of the manganese porphyrins to provide pseudo-first-order kinetics. The molar ratios of the oxidants to MnTDCSPPBr₈ and MnTSPBr₈ were about 190 and 270, respectively. Also, the quaternary ammonium groups of the supports, the binding sites for the manganese porphyrins, were in excess with respect to the amount of the manganese porphyrins. The ratios of quaternary ammonium groups to MnTDCSPPBr₈ were about 71 for CTAB, latex and 2,10-ionene and 84 for 2,6-ionene. These ratios for MnTSPBr₈ were 100 for CTAB, latex and 2,10-ionene and 116 for 2,6-ionene. Also, the reaction mixtures were buffered with appropriate buffers and the ionic strength of the reaction mixtures, except those at pH 14.1, was adjusted to 0.2 M with NaNO₃ solution. The reactions were observed using a UV-Vis spectrophotometer.

The Structural Stability of MnTDCSPPBr₈ Toward H₂O₂ and NaOCl

Although there are reports that the β -halogenated, particularly β -brominated, water-insoluble porphyrins show high resistance toward degradation by strong oxidizing agents,^{19,20} we observed rather interesting pH dependence as well as oxidant dependent stabilities of water-soluble β -brominated MnTDCSPPBr₈ and its oxidized analogue. At pH 9.5 and higher, even in the absence of oxidants, homogeneous MnTDCSPPBr₈ degraded slowly and degradation product(s) precipitated. The degradation became faster as pH increased, taking about 2 h at pH 14.1. A methanolic extract of the precipitate contained a very small amount of the unmetallated porphyrin. A solution obtained after treating the precipitate with 2 M HCl had a strong absorption band at 222 nm but no characteristic bands of porphyrin. Although Gauler et al.³² reported that the degradation products of some porphyrin-based compounds were maleimide derivatives, we did not make any further effort to characterize our degradation products. The unexpected instability of MnTDCSPPBr₈ in alkaline solutions was in contrast with the stability of its non brominated analogue, 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese (MnTDCSPP). It was briefly mentioned in the literature that MnTDCSPP was stable in alkaline and oxidant-containing solutions and its stability increased with increasing pH (especially at pH > 13) in NaOCl-containing solution¹⁴. We also carried out a detailed study of the stability of MnTDCSPP and obtained similar results³¹.

In addition to the instability of MnTDCSPPBr₈ in alkaline solutions at pH > 9.5, it also did not show considerable stability in NaOCl solutions at pH < 9.5, although its stability increased as pH decreased. At pH 2.30 and in a NaOCl solution, the Soret band of the oxidized MnTDCSPPBr₈ disappeared in approximately 30 min. In a H₂O₂-containing medium, MnTDCSPPBr₈ was much more stable than in a NaOCl medium. The degradation rate constants of homogeneous MnTDCSPPBr₈ at pH 1.60-7.20 are given in Table 1. Although MnTDCSPPBr₈ is found to be quite stable toward H₂O₂ in strongly and medium acidic solutions, it could not be oxidized with this oxidant under these conditions.

Table 1. Degradation rate constants of homogeneous and supported MnTDCSPPBr₈ in H₂O₂ at various pH's at 30°C ^a.

Exp.	Support	pH	k/min ⁻¹	λ_{\max}^b /nm
1	-	1.60	$(2.39 \pm 0.77) \times 10^{-5}$	496
2	-	4.40	$(2.02 \pm 0.49) \times 10^{-5}$	496
3	-	7.20	$(2.36 \pm 0.96) \times 10^{-4}$	491
4	CTAB	1.70	$<10^{-6}$ ^c	475
5	CTAB	4.30	$(3.45 \pm 0.66) \times 10^{-6}$	475
6	CTAB	6.70	$(1.84 \pm 0.33) \times 10^{-5}$	474
7	Latex	1.65	- ^d	461
8	Latex	4.35	$(1.98 \pm 0.49) \times 10^{-6}$	478
9	Latex	6.60	$(6.31 \pm 0.34) \times 10^{-6}$	477
10	2,6-Ionene	1.70	$(1.42 \pm 0.43) \times 10^{-5}$	502
11	2,6-Ionene	4.80	$(3.95 \pm 0.71) \times 10^{-3}$	502
12	2,6-Ionene	6.60	$(2.74 \pm 0.73) \times 10^{-4}$	501
13	2,10-Ionene	1.80	$(7.33 \pm 1.56) \times 10^{-6}$	501
14	2,10-Ionene	4.85	$(4.08 \pm 0.79) \times 10^{-3}$	501
15	2,10-Ionene	6.60	$(1.21 \pm 0.09) \times 10^{-5}$	482

^a [MnTDCSPPBr₈] = 1.04×10^{-4} M, [H₂O₂] = 0.02 M, [2,6-Ionene] = 6.04×10^{-4} M, [2,10-Ionene] = 3.22×10^{-4} M, [CTAB] = 7.44×10^{-3} M, [N⁺R₄]_{latex} = 7.44×10^{-3} M, V = 10 mL, I = 0.2 M with NaNO₃. ^b Soret maximum.

^c Calculated as $(4.6 \pm 1.9) \times 10^{-7}$ min⁻¹. ^d No change in the absorbance of the Soret band in 30 days.

As in the case of homogeneous MnTDCSPPBr₈, the CTAB-, latex- and ionene-supported MnTDCSPPBr₈ did not show considerable structural stability toward NaOCl at pH 9 and lower. On the other hand, the stabilities of CTAB- and latex-bound MnTDCSPPBr₈ in H₂O₂ solutions increased as pH decreased and their resistance to degradation increased enormously at pH < 2 (Table 1). In the latex-supported case, after 30 days, there was no decrease in the absorbance of the Soret bands within experimental error limits. Although there was a blue shift of the Soret bands of MnTDCSPPBr₈ when bound to either CTAB or the latex, we think this was due to the support effect rather than to the oxidized form of MnTDCSPPBr₈. When MnTDCSPPBr₈ was bound to the 2,6-ionene and 2,10-ionene polyelectrolytes, they showed slightly higher stabilities than their homogeneous analogue at pH < 2 (Table 1). As in the cases of the other homogeneous and supported analogues, the ionene-supported MnTDCSPPBr₈ was not oxidized with H₂O₂ and there was a slight red shift of the Soret bands of the ionene-supported MnTDCSPPBr₈ due to the matrix effect. A similar observation, a red shift of the Soret band of anionic water-soluble porphyrins induced by polyelectrolytes, was reported in the literature³³.

In summary, the stabilities of homogeneous and supported MnTDCSPPBr₈ toward H₂O₂ in acidic medium increases in the order of homogeneous < 2,6-ionene-bound < 2,10-ionene-bound << CTAB-bound < latex-bound.

Table 2. Degradation rate constants of homogeneous and supported MnTSPPBr₈ in H₂O₂ at various pH's at 30°C ^a.

Exp.	Support	pH	k/min ⁻¹	λ_{\max}^b /nm
1	-	1.50	$(1.22 \pm 0.08) \times 10^{-4}$	489
2	-	4.45	$(4.67 \pm 0.70) \times 10^{-5}$	482
3	-	6.65	$(3.59 \pm 0.38) \times 10^{-2}$	491
4	CTAB	1.60	$(5.41 \pm 0.51) \times 10^{-6}$	495
5	CTAB	4.25	$(1.04 \pm 0.05) \times 10^{-5}$	495
6	CTAB	5.10	$(4.45 \pm 0.66) \times 10^{-3}$	495
7	CTAB	6.60	$(1.22 \pm 0.30) \times 10^{-2}$	472
8	Latex	1.65	- ^c	471
9	Latex	4.25	$(8.80 \pm 1.12) \times 10^{-5}$	481
10	Latex	6.60	$(2.68 \pm 0.26) \times 10^{-3}$	481
11	2,6-Ionene	1.70	$(5.03 \pm 1.30) \times 10^{-5}$	504
12	2,6-Ionene	4.30	$(7.07 \pm 1.69) \times 10^{-5}$	485
13	2,6-Ionene	6.60	$(2.57 \pm 0.17) \times 10^{-3}$	504
14	2,10-Ionene	1.65	$(8.41 \pm 0.81) \times 10^{-5}$	492
15	2,10-Ionene	5.10	$(4.45 \pm 0.66) \times 10^{-3}$	491
16	2,10-Ionene	6.60	$(1.05 \pm 0.24) \times 10^{-2}$	491

^a [MnTSPPBr₈] = 7.46×10^{-5} M, [H₂O₂] = 0.02 M, [2,6-Ionene] = 6.04×10^{-4} M, [2,10-Ionene] = 3.22×10^{-4} M, [CTAB] = 7.44×10^{-3} M, [N⁺R₄]_{latex} = 7.44×10^{-3} M, V = 10 mL, I = 0.2 M with NaNO₃. ^b Soret maximum. ^c No change in the absorbance of the Soret band in 6 days.

The Structural Stability of MnTSPPBr₈ Toward H₂O₂ and NaOCl

A trend similar to the case of MnTDCSPPBr₈ was observed for the structural stabilities of homogeneous and bound MnTSPPBr₈. At pH 10.5 and higher, MnTSPPBr₈ degraded and precipitated in solutions in the absence of any oxidant. In NaOCl solutions at pH 1-9.25, MnTSPPBr₈ was not stable at all and degraded

in less than 5 min. The supported MnTSPBr₈ showed similar behaviour in NaOCl-containing solutions. On the other hand, homogeneous MnTSPBr₈ showed considerable stability toward H₂O₂ in this pH range, although lower than that of MnTDCSPPBr₈ under similar conditions (Table 2). The Soret band disappeared after 2 min at pH 9.25 while 38% of MnTSPBr₈ was intact after 6 days at pH 1.50. Moreover, H₂O₂ was not able to oxidize MnTSPBr₈ at this pH. After the binding of MnTSPBr₈ to CTAB and the latex, its stability toward H₂O₂ increased greatly at low pH (Table 2). At pH < 2, no degradation of latex-bound MnTSPBr₈ and very slow degradation of CTAB-bound MnTSPBr₈ was observed. When bound to 2,6-ionene and 2,10-ionene, MnTSPBr₈ showed higher stabilities toward H₂O₂ than the homogeneous analogue but much lower stabilities than the CTAB- and latex-bound MnTSPBr₈.

The stabilities of homogeneous and bound MnTSPBr₈ toward H₂O₂ in acidic medium increased in the order of homogeneous < 2,10-ionene-bound < 2,6-ionene-bound << CTAB-bound << latex-bound.

Conclusion

The β -brominated water-soluble MnTDCSPPBr₈ and MnTSPBr₈ were not stable in alkaline solutions even in the absence of any oxidant and in NaOCl-containing solutions at pH < 9. Both manganese porphyrins showed increasing structural stabilities toward H₂O₂ as pH decreased but they were not oxidized by H₂O₂. When both the manganese porphyrins were bound to latex and CTAB supports, almost no degradation by H₂O₂ was observed at low pH. Both the homogeneous and supported MnTDCSPPBr₈ were more stable in H₂O₂ solutions than the homogeneous and supported MnTSPBr₈.

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