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Structural stabilities of sulfonated manganese tetramesitylporphyrin and its β-brominated analogue toward NaOCl, H_2O_2 and $(CH_3)_3COOH$

Hayrettin Türk *, Turgay Tay, Hüseyin Berber

Department of Chemistry, Faculty of Sciences, Anadolu University, 26470 Eskişehir, Turkey

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Abstract

This article gives the degradation rate constants of *meso*-tetrakis(3,5-disulfonatomesityl)porphinatomanganese(III) X (where X = H_2O and/or OH^- depending on pH) (MnTMSP) and its β-brominated analogue ($MnTMSPBr_8$) toward the oxidants NaOCl, H_2O_2, and $(CH_3)_3COOH$ at various pHs, $I = 0.2$ M and 30°C. In addition, the degradation rate constants of MnTMSP was determined when it was bound to cationic supports — namely, CTAB, a poly(vinylbenzyltrimethylammonium chloride) latex, 2,6-ionene and 2,10-ionene. MnTMSP showed high structural stability toward the peroxides in strong acidic medium and the degradation rate constants were found as low as 10^{-4} min^{-1} at pH < 1.50. When NaOCl was employed as the oxidant, the pH dependence of the stability of MnTMSP was vice versa and its degradation rate constant was determined as 1.43×10^{-4} min^{-1} at pH 14.10. In strong acidic solution, the supports CTAB and latex made the stability of MnTMSP toward the peroxides improve significantly. In strong basic solution, only latex-bound MnTMSP showed higher stability toward NaOCl than the homogeneous MnTMSP. Because $MnTMSPBr_8$ was not stable in solutions having pH higher than 9 and containing no oxidant, its stability was investigated at pH < 9 and it showed slightly lower stability toward the peroxides than the non-brominated analogue. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Porphyrin stability; Porphyrin degradation; Tetramesitylporphyrin Supported porphyrin

1. Introduction

After the discovery of the cyctochrome *P*-450 monooxygenese-like activity of *meso*-tetraphenylporphinatoiron(III) chloride in 1979, a large class of metalloporphyrins were synthesized and used as catalysts for epoxidation and hydroxylation reactions [1–6]. Although many advances have been made concerning the selectivities and mechanisms of these oxidations [3–22], it was found that metalloporphyrin catalysts are not very stable during the reactions. They act frequently as a substrate and self-destruct in an intermolecular process. Also, it has been well established that the stability of a porphyrin depends on the substituents on the phenyl and pyrrole moities of the macrocycle as well as the

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* Corresponding author. Tel.: +90-222-335-0581, ext. 5122; fax: +90-222-320-4910.

E-mail address: hturk@anadolu.edu.tr (H. Türk).

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nature of the oxidizing species. However, there are only a few reports in the literature dealing specifically with the stabilities of the porphyrins and their metallo derivatives [22–30]. In general, electron-withdrawing and bulky substituents especially in the *ortho*-positions of the phenyl groups were enhancing the stabilities of the porphyrins [16,17,24–27,31]. Also, halogens at the β-pyrrole carbons are believed to increase the porphyrin stability more. Hoffmann et al. found that manganese tetramesitylporphyrins containing chlorines or bromines at the β-pyrrole carbons were better catalysts and more robust than manganese tetramesitylporphyrin [16]. Also, they observed higher catalytic activities for the sulfonated and β-halogenated manganese tetramesitylporphyrin with respect to those of the sulfonated manganese tetramesitylporphyrin [17]. Banfi et al. reported that halogenation of β-pyrrole carbons of some tetraarylporphyrins decreased the robustness as well as reactivitiy of these catalysts with respect to the unsubstituted analogues, except manganese tetramesityl-β-octabromoporphyrin, that proved to be more efficient catalyst than the nonbrominated analogue [22]. Also, it has been reported that bromines 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 [31,32].

Furthermore, nearly all of the reports in the literature evaluate the porphyrin stability under reaction conditions in which oxidant, metalloporphyrin, substrate and some other constituents, such as phase transfer catalyst, axial ligand, are present. Under reaction conditions, metalloporphyrins were protected by a large excess of substrate present in the reaction mixture and oxidants were generally used equal or slightly excess amount with respect to the metalloporphyrins. In addition, the reactions usually employ a water-soluble oxidant and a water-insoluble metalloporphyrin as a catalyst and need to be carried out in a two-phase system where the water-soluble oxidants are partitioned in the organic phase at a concentration that is much lower than that of in the aqueous phase. However, that may not be true under the two-phase conditions and using high substrate-porphyrin and equal or low oxidant-porphyrin ratios, where the stabilities of the metalloporphyrins may appear to be quite high.

This study has been carried out to determine the degradation rate constants and eventually the structural stabilities of *meso*-tetrakis(3,5-disulfonatomesityl)porphinatomanganese(III) X (where $X = H_2O$ and/or OH^- depending on pH) and *meso*-tetrakis(3,5-disulfonatomesityl)-β-octabromoporphinatomanganese(III) X (where $X = H_2O$ and/or OH^- depending on pH) when NaOCl, H_2O_2, and $(CH_3)_3COOH$ were employed as the oxidant (Fig. 1). By choosing these water-soluble manganese porphyrins instead of their water-insoluble analogues, we had a system in which the manganese porphyrins and oxidants were in the same phase. Also, we did not add any substrate, any axial ligand, any phase transfer catalyst to the reaction mixture to avoid their influences on the structural stabilities of these porphyrins. Also, we were interested in finding the influences of the supports — namely 2,6-ionene, 2,10-ionene, hexadecyltrimethylammonium bromide (CTAB), and a quaternary ammonium containing latex — on the structural stabilities of these manganese por-

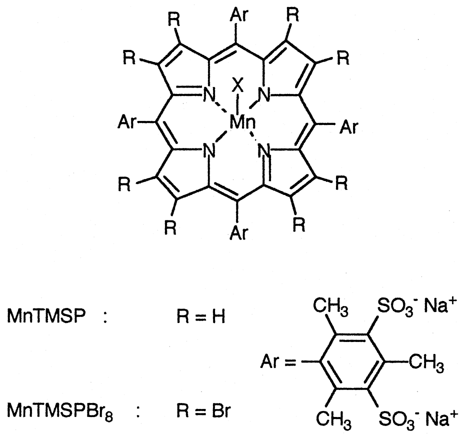

Fig. 1. Structures of the manganese porphyrins.

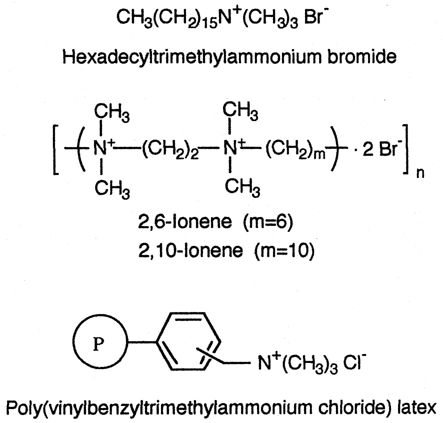

Fig. 2. Structures of the supports.

phyrins when they were attached to them (Fig. 2).

2. Experimental

2.1. Materials and instrumentation

UV–visible spectra were recorded on a Shimadzu UV-2101 PC spectrophotometer equipped with thermostated cell holders at 30°C. Chemicals were analytical grade and purchased from Aldrich, Merck or Fluka. The solvents used were fractional distilled before use. *meso*-Tetramesitylporphyrin (H_2TMP) was prepared and purified according to the published methods [16,33] and its β-brominated analogue, H_2TMPBr_8, was obtained with NBS as described by Hoffmann et al. [16,34]. The sulfonations of H_2TMP and H_2TMPBr_8 were performed with fuming H_2SO_4 (18–24% SO_3) according to the published methods [17,34]. The manganese complex of H_2TMSP was prepared with $MnCl_2$ in pH 8.5–9.0 solution at 85°C for 40 h while that of $H_2TMSPBr_8$ was prepared with $MnCl_2$ in pH 6.0–6.5 solution at 85°C for 20 h.

Poly(vinylbenzyltrimethylammonium chloride) latex was from a previous work [35]. It was 5% cross-linked and contained 3.58×10^{-3} eq quaternary ammonium group per gram. The average particle size of the latex determined from TEM micrographs was 66 ± 16 nm. 2,6-Ionene and 2,10-ionene were prepared using a modified German method [36]. The numbers of the average molecular weights (M_n) were 2700 for 2,6-ionene and 4900 for 2,10-ionene, respectively and were determined by titration with sodium hydroxide after converting their amine-terminated end groups to quaternary ammonium groups with hydrochloric acid [36]. These M_ns correspond to 14.4 and 23.0 quaternary ammonium groups per molecule, respectively.

2.2. General procedure for the determination of the chemical stabilities of MnTMSP and $MnTMSPBr_8$

The changes of the absorption spectra of MnTMSP and $MnTMSPBr_8$ in the presence of H_2O_2, $(CH_3)_3COOH$, and NaOCl at various pHs were followed and the decrease of their absorbances of the Soret bands at λ_{max} were used to calculate the degradation rates constants. The procedure was similar to the one employed for the determination of the stabilities of *meso*-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) X (MnTDCSPP) and *meso*-tetra(4-sulfonatophenyl)porphinatomanganese(III) X (MnTSPP) which is described elsewhere [37].

3. Results and discussion

3.1. The structural stabilities of MnTMSP and $MnTMSPBr_8$

The structural stabilities of the homogeneous MnTMSP and $MnTMSPBr_8$ and their supported analogues were investigated toward H_2O_2, $(CH_3)_3COOH$ and NaOCl throughout the pH range at $I = 0.2$ M and 30°C. Using the pseudo-first-order rate law, their degradation rate constants and uncertainties were calculated. These oxidants are commonly used as an oxygen source in the metalloporphyrin catalyzed oxidations and hydroxylations. During the experiments, we employed high oxidant concentrations relative to those of the manganese porphyrins to provide pseudo-first-order kinetics. The relative molar ratios of H_2O_2 and $(CH_3)_3$-COOH to the manganese porphyrins were about 360. When NaOCl was employed, the oxidant-manganese porphyrin ratio was 720. Also the number of quaternary ammonim groups of the supports which were the binding sites for the manganese porphyrins were in excess respect to the number of the manganese porphyrins. The ratios of quaternary ammonium groups to the manganese porphyrins were about 134 for CTAB, latex and 2,10-ionene and 157 for 2,6-ionene. Also reaction mixtures were buffered with appropriate buffers and the ionic strength of the reaction mixtures, except the ones at pH 14.1, was adjusted to 0.2 M with $NaNO_3$ solution. The reactions were followed by using a UV–Vis spectrophotometer.

Table 1
The pH dependence of the degradation rate constants of homogeneous MnTMSP[a]

Experiment	Oxidant[b]	pH	k ($\min^{-1}$)	λ^{c}_{max} (nm)
1	H_2O_2	1.25	$(5.40 \pm 0.35) \times 10^{-5}$	468
2	H_2O_2	4.70	$(6.80 \pm 0.34) \times 10^{-5}$	468
3	H_2O_2	9.20	$(9.42 \pm 0.55) \times 10^{-2}$	468
4	H_2O_2	11.50	–[d]	468
5	H_2O_2	12.90	$(7.95 \pm 1.71) \times 10^{-2}$	427
6	H_2O_2	14.10	$(1.13 \pm 0.07) \times 10^{-2}$	427
7	$(CH_3)_3COOH$	1.35	$(7.11 \pm 0.30) \times 10^{-5}$	468
8	$(CH_3)_3COOH$	4.85	$(4.35 \pm 0.29) \times 10^{-5}$	468
9	$(CH_3)_3COOH$	9.40	$(8.73 \pm 0.69) \times 10^{-3}$	468
10	$(CH_3)_3COOH$	11.75	$(7.76 \pm 0.38) \times 10^{-3}$	468
11	$(CH_3)_3COOH$	12.95	$(3.54 \pm 0.25) \times 10^{-2}$	426
12	$(CH_3)_3COOH$	14.10	$(1.16 \pm 0.08) \times 10^{-2}$	427
13	NaOCl	1.30	$(9.30 \pm 1.49) \times 10^{-3}$	417
14	NaOCl	4.85	–[e]	421
15	NaOCl	6.30	–[e]	421
16	NaOCl	10.20	(0.196 ± 0.019)	421
17	NaOCl	11.90	$(1.18 \pm 0.02) \times 10^{-2}$	426
18	NaOCl	12.90	$(2.89 \pm 0.97) \times 10^{-4}$	418
19	NaOCl	14.10	$(1.43 \pm 0.13) \times 10^{-4}$	418

[a] $[MnTMSP] = 5.54 \times 10^{-5}$ M; $[H_2O_2] = 0.02$ M; $[(CH_3)_3COOH] = 0.02$ M; $[NaOCl] = 0.04$ M; $t = 30°C$; $V = 10$ ml; $I = 0.2$ M with $NaNO_3$ (at pH 14.10, I was 1.2 M).

[b] OCl^- is in the form of HOCl in acidic solutions.

[c] The Soret maximum.

[d] Degraded in 1 min.

[e] Degraded in 3 min.

3.2. The structural stability of MnTMSP toward H_2O_2, $(CH_3)_3COOH$ and NaOCl

The stability of MnTMSP was found to depend on the type of oxidant used, the pH of the medium and the support, if present. The degradation of homogeneous MnTMSP by H_2O_2 and $(CH_3)_3COOH$ showed strict pH dependence (Table 1). The degradation rate constants toward both oxidants were lower than 1×10^{-4} $\min^{-1}$ at $\text{pH} < 1.50$ and increased as the pH increased. In neutral and slightly basic medium, the stability of MnTMSP, especially toward H_2O_2, was almost none. Again, MnTMSP showed some stability toward both peroxides in strong basic medium and its degradation rate constants at pH 14.10 were in the order of 10^{-2} $\min^{-1}$. Both peroxides were able to oxidize MnTMSP only at pH higher than 12.5. When NaOCl was employed as the oxidant, the pH dependence of the stability of homogeneous MnTMSP was vice versa that of when the peroxides were used (Table 1). The degradation rate constant of MnTMSP toward NaOCl was calculated as 1.43×10^{-4} $\min^{-1}$ at pH 14.10. In the mid-pH range, MnTMSP degraded very fast as in the case when the peroxides were employed. In slightly acidic solutions, we did not observe any stability of MnTMSP toward HOCl ($pK_a = 7.53$) which is the major form of OCl^- in acidic solutions. MnTMSP showed again some stability in strong acidic soltions and the degradation rate constant at pH 1.30 was calculated as 9.30×10^{-3} $\min^{-1}$. It is reasonable that MnTMSP should show relatively high stability toward NaOCl in strong basic medium in which the concentration of HOCl is very low. HOCl, which is a powerful oxidant, is thought to be responsible for the destruction of porphyrin ligand when NaOCl is employed as the oxidant and these results are in agreement with reports which mention the high stability of

Table 2
The pH dependence of the degradation rate constants of CTAB-bound MnTMSP[a,b]

Experiment	Oxidant[c]	pH	k (min^{-1})	λ^{d}_{max} (nm)
1	H_2O_2	1.30	–[e]	482
2	H_2O_2	4.65	–[e]	471
3	H_2O_2	9.25	$(2.99 \pm 0.09) \times 10^{-2}$	472
4	$(CH_3)_3COOH$	1.40	–[f]	482
5	$(CH_3)_3COOH$	4.80	–[f]	471
6	$(CH_3)_3COOH$	9.45	$(1.09 \pm 0.07) \times 10^{-2}$	428
7	$(CH_3)_3COOH$	11.65	$(1.63 \pm 0.25) \times 10^{-2}$	427
8	NaOCl	5.95	$(2.70 \pm 0.43) \times 10^{-2}$	418
9	NaOCl	9.90	$(2.81 \pm 0.29) \times 10^{-3}$	422
10	NaOCl	11.85	$(2.54 \pm 0.19) \times 10^{-3}$	426
11	NaOCl	14.10	$(1.28 \pm 0.04) \times 10^{-3}$	422

[a] $[MnTMSP] = 5.54 \times 10^{-5}$ M; $[H_2O_2] = 0.02$ M; $[(CH_3)_3COOH] = 0.02$ M; $[NaOCl] = 0.04$ M; $t = 30$°C; $V = 10$ ml; $I = 0.2$ M with $NaNO_3$ (at pH 14.10, I was 1.2 M).

[b] $[CTAB] = 7.44 \times 10^{-3}$ M.

[c] OCl^- is in the form of HOCl in acidic solutions.

[d] The Soret maximum.

[e] No change in the absorbance intensity of the Soret band in 12 days.

[f] No change in the absorbance intensity of the Soret band in 2 days.

MnTDCSPP toward NaOCl at pH > 13. In addition, NaOCl or HOCl was able to oxidize MnTMSP throughout the pH range.

When MnTMSP was bound to the supports CTAB and latex, both supports made the stability of MnTMSP improve significantly. The resistance of CTAB-bound MnTMSP toward degradation by H_2O_2 and $(CH_3)_3COOH$ increased enormously at $pH < 5$ and practically no degradation of the manganese porphyrin by both oxidants was observed (Table 2). On the contrary to the improved stability of CTAB-bound MnTMSP toward the peroxides in acidic solutions, low stability toward NaOCl was observed in strong basic solutions: it was even lower than that of the homogeneous analogue. Kadish et al. found that *meso*-tetra(4-sulfonatophenyl)porphyrin and its zinc analogue are intercalated in CTAB and reside in a more hydrophobic environment [38]. We expect MnTMSP, which is more hydrophobic than the above porphyrins due to having 12 CH_3 groups on the structure, to reside inside the CTAB micelles and the high resistance of MnTMSP toward the peroxides can be accounted for the low concentrations of the peroxides in the hydrophobic micellar environment. This is because the partitions of the peroxides in the micellar environment where the porphyrin resides should be low as compared to their concentrations in aqueous environment. The low stability of CTAB-bound MnTMSP toward NaOCl can be attributed to lower pH of the micellar environment than that of aqueous solution. At low pH, HOCl, the acidic form of OCl^-, forms inside the micelle and/or penetrates into. We expect this pH decrease inside the micelle to cause HOCl formation and to eventually lead to quick destruction of MnTMSP.

In the latex supported case, MnTMSP showed high stability toward H_2O_2 and $(CH_3)_3COOH$ in acidic medium and toward NaOCl in strong basic medium (Table 3). No degradation of the

Table 3
The pH dependence of the degradation rate constants of the latex-bound MnTMSP[a,b]

Experiment	Oxidant[c]	pH	k (min^{-1})	λ^{d}_{max} (nm)
1	H_2O_2	1.30	$(5.70 \pm 1.78) \times 10^{-6}$	482
2	H_2O_2	4.85	$(8.05 \pm 0.32) \times 10^{-6}$	471
3	H_2O_2	9.20	$(2.74 \pm 0.12) \times 10^{-2}$	473
4	H_2O_2	11.65	(0.119 ± 0.019)	428
5	$(CH_3)_3COOH$	1.35	–[e]	482
6	$(CH_3)_3COOH$	4.75	$(3.79 \pm 0.47) \times 10^{-5}$	471
7	$(CH_3)_3COOH$	9.35	$(6.30 \pm 0.45) \times 10^{-2}$	425
8	$(CH_3)_3COOH$	11.65	(0.133 ± 0.008)	428
9	$(CH_3)_3COOH$	13.20	(0.118 ± 0.016)	428
10	NaOCl	6.30	(0.252 ± 0.007)	412
11	NaOCl	10.40	$(2.98 \pm 0.34) \times 10^{-2}$	422
12	NaOCl	11.90	$(8.00 \pm 0.64) \times 10^{-3}$	426
13	NaOCl	14.10	–[f]	425

[a] $[MnTMSP] = 5.54 \times 10^{-5}$ M; $[H_2O_2] = 0.02$ M; $[(CH_3)_3COOH] = 0.02$ M; $[NaOCl] = 0.04$ M; $t = 30$°C; $V = 10$ ml; $I = 0.2$ M with $NaNO_3$ (at pH 14.10, I was 1.2 M).

[b] $[N^+R_4]_{latex} = 7.40 \times 10^{-3}$ M.

[c] OCl^- is in the form of HOCl in acidic solutions.

[d] The Soret maximum.

[e] No change in the absorbance intensity of the Soret band in 2 days.

[f] No change in the absorbance intensity of the Soret band in 4 days.

latex-supported MnTMSP by $(CH_3)_3COOH$ at pH 1.35 and by NaOCl at pH 14.10 was observed. As in the CTAB-bound case, MnTMSP should be embedded in the latex particles and protected by the attacks of the oxidants. The stability of latex-bound MnTMSP toward both peroxides at lower pH is quite similar to that of the CTAB-bound analogue. However, its stability toward NaOCl is very high as compared to the stability of CTAB-bound MnTMSP. Similar results for the high stability of latex-bound MnTDCSPP toward NaOCl, even higher than the homogeneous analogue, were reported [27,37].

The structural stabilities of 2,6-ionene and 2,10-ionene-bound MnTMSPs showed similar stability trend as that of homogeneous MnTMSP and the degradation rate constants of 2,6- and 2,10-ionene-bound MnTMSPs toward H_2O_2 were close to that of homogeneous MnTMSP under similar conditions (Table 4). When NaOCl was employed as the oxidant, the ionene supports affected the stability of MnTMSP adversely at high pH. Since the ionenes are low molecular weight supports and are expected to be extended in the solution, it is reasonable that their influences on the stability of MnTMSP should be minimal and close to the stability of homogeneous MnTMSP.

As a result, the stability of MnTMSP was affected primarily by the type of oxidant and the pH of the medium, and in some extent by the type of the support used. In summary, the order of the stabilities of homogeneous and bound MnTMSP toward H_2O_2 and $(CH_3)_3COOH$ in strong acidic medium changes as CTAB-bound $\geq$ latex-bound $\gg$ 2,10-ionene-bound $>$ homogeneous $>$ 2,6-ionene-bound and toward NaOCl in strong basic medium changes as latex-bound $>$ homogeneous $>$ CTAB-bound $>$ 2,10-ionene-bound $>$ 2,6-ionene-bound.

3.3. The structural stability of $MnTMSPBr_8$ toward H_2O_2, $(CH_3)_3COOH$ and NaOCL

During the study of the stability of $MnTMSPBr_8$, we interestingly observed that $MnTMSPBr_8$ does not have any stability in

Table 4
The pH dependence of the degradation rate constants of ionene-bound MnTMSPs[a,b]

Experiment	Support	Oxidant[c]	pH	k (min^{-1})	λ_{max}^{d} (nm)
1	2,6-ionene	H_2O_2	1.20	$(6.58 \pm 0.68) \times 10^{-5}$	469
2	2,6-ionene	H_2O_2	4.80	$(4.54 \pm 0.34) \times 10^{-5}$	469
3	2,6-ionene	H_2O_2	9.25	$(3.98 \pm 0.37) \times 10^{-2}$	469
4	2,6-ionene	H_2O_2	12.15	(0.160 ± 0.036)	425
5	2,10-ionene	H_2O_2	1.45	$(3.83 \pm 0.40) \times 10^{-5}$	470
6	2,10-ionene	H_2O_2	4.70	$(4.52 \pm 0.60) \times 10^{-5}$	470
7	2,10-ionene	H_2O_2	9.25	$(3.58 \pm 0.34) \times 10^{-2}$	470
8	2,10-ionene	H_2O_2	12.20	(0.109 ± 0.007)	425
9	2,6-ionene	NaOCl	5.95	(0.109 ± 0.017)	425
10	2,6-ionene	NaOCl	10.30	$(3.02 \pm 0.39) \times 10^{-2}$	423
11	2,6-ionene	NaOCl	11.90	$(9.68 \pm 0.83) \times 10^{-3}$	421
12	2,6-ionene	NaOCl	12.85	$(7.16 \pm 0.54) \times 10^{-3}$	426
13	2,10-ionene	NaOCl	5.90	$(6.88 \pm 1.24) \times 10^{-2}$	414
14	2,10-ionene	NaOCl	10.30	(0.122 ± 0.007)	424
15	2,10-ionene	NaOCl	11.90	$(4.38 \pm 0.99) \times 10^{-2}$	427
16	2,10-ionene	NaOCl	12.90	$(2.12 \pm 0.20) \times 10^{-2}$	422
17	2,10-ionene	NaOCl	14.10	$(8.12 \pm 0.13) \times 10^{-3}$	423

[a] $[MnTMSP] = 5.54 \times 10^{-5}$ M; $[H_2O_2] = 0.02$ M; $[(CH_3)_3COOH] = 0.02$ M; $[NaOCl] = 0.04$ M; $t = 30°C$; $V = 10$ ml; $I = 0.2$ M with $NaNO_3$ (at pH 14.10, I was 1.2 M).

[b] $[2,6\text{-Ionene}] = 6.04 \times 10^{-4}$ M, $[2,10\text{-Ionene}] = 3.22 \times 10^{-4}$ M.

[c] OCl^- is in the form of HOCl in acidic solutions.

[d] The Soret maximum.

solutions having pH higher than 9 and containing no oxidant. Our ongoing research on the stabilities of β-brominated water soluble manganese porphyrins revealed similar instability behaviors for *meso*-tetrakis(2,6-dichloro-3-sulfonatophenyl)-β-octabromoporphinatomanganese(III) X and *meso*-tetra(4-sulfonatophenyl)-β-octabromoporphinatomanganese(III) X in basic solutions as well. When we brought the pH of the $MnTMSPBr_8$ solution to 9.0 or a higher pH, a red insoluble material gradually formed and precipitated. The aqueous phase was clear and did not contain any porphyrin. The precipitate was soluble neither in dichloromethane nor in methanol. When the precipitate was treated with 2 M HCl, it was partly soluble. The UV–Vis spectrum of the soluble part showed a strong absorption band at 220–225 nm and no characteristic absorption bands for the porphyrin. Thus we concluded that $MnTMSPBr_8$ is self- or base-catalyzed destructed in basic medium and did not pursue to characterize the degradation products of $MnTMSPBr_8$. However, the degradation products of some porphyrin-based compounds were reported as maleimide derivatives [39].

Due to the instability of $MnTMSPBr_8$ in strong basic solutions, we studied its stability toward NaOCl, H_2O_2, and $(CH_3)_3COOH$ in solutions having pH lower than 9. $MnTMSPBr_8$ showed almost no stability toward NaOCl until pH was very low. The rate constants determined at pH 1.20 is 2.58×10^{-2} min^{-1} (Table 5). In contrary to low stability of $MnTMSPBr_8$ toward NaOCl, it showed much higher stability toward H_2O_2 and $(CH_3)_3COOH$ and its stability increased as the pH went down (Table 5). The degradation rate constants of $MnTMSPBr_8$ toward both peroxides at pH 1.25 are roughly in the order of 10^{-4} min^{-1}. Both oxidants were not able to oxidize $MnTMSPBr_8$ in the studied pH range. We did not attempt to determine the stabilities of the ionene, CTAB and the latex-bound $MnTMSPBr_8$ because the stability of homogeneous $MnTMSPBr_8$ toward the peroxides was lower than that of MnTMSP under similar conditions. Thus, we expect similar stability trend but not higher stability behavior for the supported $MnTMSPBr_8$ as in the case of the supported MnTMSP.

Table 5
The pH dependence of the degradation rate constants of homogeneous $MnTMSPBr_8^a$

Experiment	Oxidant[b]	pH	k (min^{-1})	λ_{max}^c (nm)
1	H_2O_2	1.25	$(8.74 \pm 2.03) \times 10^{-5}$	496
2	H_2O_2	3.95	$(1.12 \pm 0.16) \times 10^{-4}$	496
3	H_2O_2	4.75	$(2.96 \pm 0.14) \times 10^{-4}$	496
4	$(CH_3)_3COOH$	1.25	$(1.14 \pm 0.14) \times 10^{-4}$	497
5	$(CH_3)_3COOH$	3.95	$(4.53 \pm 0.43) \times 10^{-4}$	497
6	$(CH_3)_3COOH$	4.65	$(1.07 \pm 0.16) \times 10^{-3}$	496
7	NaOCl	1.20	$(2.58 \pm 0.68) \times 10^{-2}$	496

[a] $[MnTMSPBr_8] = 5.54 \times 10^{-5}$ M; $[H_2O_2] = 0.02$ M; $[(CH_3)_3COOH] = 0.02$ M; $[NaOCl] = 0.04$ M; $t = 30°C$; $V = 10$ ml; $I = 0.2$ M with $NaNO_3$ (at pH 14.10, I was 1.2 M).

[b] OCl^- is in the form of HOCl in acidic solutions.

[c] The Soret maximum.

4. Conclusions

Water soluble manganese tetramesitylporphyrin showed higher resistance toward the oxidants than its octabrominated analogue. In addition, the $MnTMSPBr_8$ was not stable in strong basic solutions even in the absence of any oxidant where MnTMSP showed some stability toward the oxidants. The supports make some influence on the stability of MnTMSP; however, they do not alter its stability. In contrary to general belief, β-bromination helping increase porphyrin stability is not true for the water soluble manganese tetramesitylporphyrin.

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