

Oxidation of dyes by manganese tetraphenyl porphyrin activated peroxy bleach

R G BHIRUD, E V SRISANKAR and K S NARAYAN*

Hindustan Lever Research Centre, ICT Link Road, Sahar P.O., Andheri (East), Bombay 400 099, India

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Abstract. The oxidation of a number of dyes in predominantly aqueous systems by tetraphenylporphyrinato manganese(III) imidazole, MnTPP(Im), activated peroxy bleach has been studied in the context of application in detergent systems. Dyes with an olefinic linkage in the chromophoric group are readily oxidized by perborate even in the absence of the activator. On the other hand, dyes with an azo linkage are resistant to oxidation and are bleached only to a limited extent (25%) even by MnTPP(Im) activated perborate. In the presence of a surfactant, alkylbenzene sulphonate, bleaching is further inhibited by micellar solubilization of the dyes. Sulphonation of MnTPP(Im) only marginally improves the bleaching efficiency in presence of the surfactant. MnTPP(Im) is also destroyed by perborate in the absence of the substrate. In view of these limitations, the metalloporphyrin activated peroxy bleach system is not promising for application in detergent systems. Attempts have also been made to explain the difference in the behaviour of different substrates on structural consideration.

Keywords. Bleaching; oxidation; dyes; perborate; Mn-porphyrin; alkylbenzene sulphonate; micellar effects.

1. Introduction

Transition metal complex mediated oxidation processes are receiving attention in recent times. This concept is based on the analogy with cytochrome P-450 whose key feature is the involvement of a metalloporphyrin complex (Coon and White 1980; Guengerich and MacDonald 1985). The oxidation of olefins to epoxides (White and Coon 1980; Collman *et al* 1985), alkanes to alcohols (Guengerich and MacDonald 1984), dialkylamines to amine oxides (Poulos *et al* 1985) with oxygen supply from an exogenous source has given a lot of impetus to work on model systems using metalloporphyrins. High valent metalloporphyrin oxidizing species have been obtained with iron (Groves *et al* 1981), manganese (Hill and Schardt 1980) and chromium (Groves and Haushalter 1981). Most of the studies reported employ oxygen donors such as alkylhydroperoxide, peracids, iodosylbenzene, amine oxide, persulphate (Collman *et al* 1985; Depoorter and Meunier 1985; Groves and Quinn 1985; Renaud *et al* 1985). Invariably two-phase systems have been employed with the oxidant in the

*For correspondence

aqueous phase while the non-aqueous phase contains metalloporphyrin and the substrate along with a phase transfer catalyst.

We thought it would be worthwhile examining the versatility of the metalloporphyrin mediated peroxy bleach system by studying the bleaching of dyes in predominantly aqueous systems by manganese porphyrins. A range of dyes with different reactive groups such as azo, olefinic and different structural features have been selected. Bleaching experiments have been carried out in two solvent systems and also in a micellar system to delineate the behaviour in these systems. We also wanted to examine the applicability of this bleaching principle to detergent systems and have, therefore, used sodium perborate, a common bleaching agent in detergent systems as the oxygen donor and linear alkylbenzene sulphonate (LAS), a versatile surfactant used in detergents. We also felt that it would be of interest to study the effect of solubilizing the metalloporphyrin through sulphonation.

2. Experimental

2.1 Chemicals

Imidazole, direct yellow-9, rhodamine 6G, 4-nitrophenyl-azoresorcinol, *p*-dimethylamino benzylidenerhodanine, carmine AS, carmine MS were obtained from BDH, England. Direct red-23, direct red-81, quinaldine blue, quinaldine red, *m*-chloroperbenzoic acid were obtained from Sigma or Aldrich. Eriochrome blue black, eriochrome black T, methyl orange, methyl red and fuchsin basic were from Merck. Sunset yellow and tartrazine were cosmetic grade dyestuffs (ex Devarsons Limited). Structures of the various dyes are given in figure 1. 5, 10, 15, 20-tetraphenylporphyrin (TPP) and tetraammonium tetra (*p*-sulphophenyl) porphyrin (TPPS) were obtained from Organic Chemistry Section, HLRC. Linear alkylbenzene sulphonate (LAS), sodium tripolyphosphate (STP) and sodium carbonate were commercial samples. Dimethylformamide (DMF) and methanol were of reagent grade ex E. Merck. Distilled water was used for preparation of solutions.

2.2 Preparation

2.2a (5, 10, 15, 20 Tetraphenylporphyrinato) manganese(III) acetate (MnTPP)(OAC): Manganese(II) acetate tetrahydrate (2 gms) and tetraphenyl porphyrin (0.5 gms) were dissolved in 100 ml of DMF and the solution was refluxed for 5–6 hours. DMF was

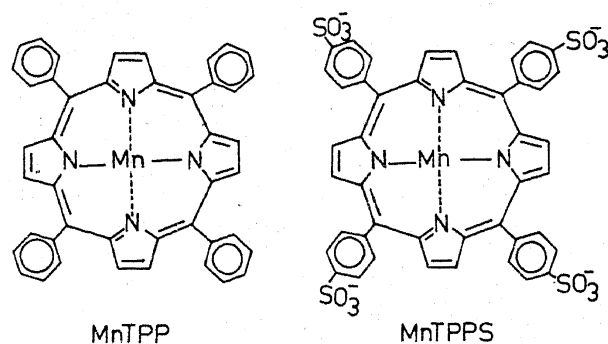


Figure 1(a). Structure of MnTPP and MnTPPS(S).

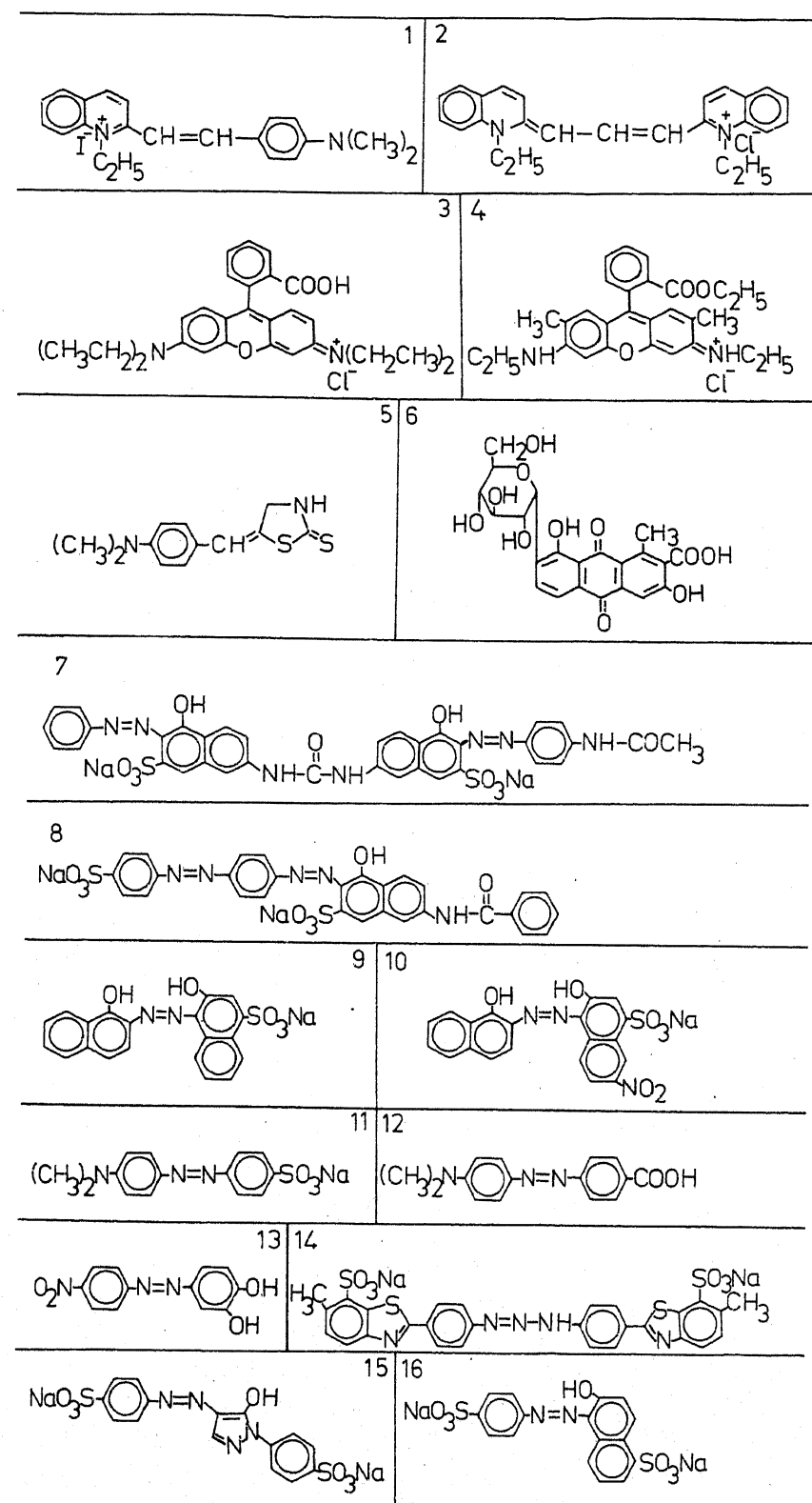


Figure 1(b). Structure of dyes used in the studies: (1) quinaldine red, (2) quinaldine blue, (3) rhodamine B, (4) rhodamine 6G, (5) *p*-dimethyl amino benzylidene rhodanine, (6) carminic acid, (7) direct red-23, (8) direct red-81, (9) eriochrome blue black, (10) eriochrome black T, (11) methyl orange, (12) methyl red, (13) 4-nitrophenylazo resorcinol, (14) direct yellow 9, (15) tartrazine, (16) sunset yellow.

removed using a high vacuum rotary evaporator. The dried reaction mixture was then slurried in sodium acetate solution and extracted with chloroform. After shaking for several minutes, the aqueous phase was separated. Chloroform layer was taken in a rotary evaporator to remove the solvent. The final product was again extracted with chloroform in a Soxhlet thimble and recrystallised. The preparation was as per Adler *et al* (1970).

2.2b Tetra (*p*-sulphophenylporphyrinato) manganese(III) acetate (MnTPPS): 50 mg tetra (*p*-sulphophenyl) porphyrin and 200 mg manganous acetate tetrahydrate were stirred in 100 ml methanol at 40–50°C for three hours. The solution was then kept overnight in the dark. The solution after ageing was filtered and concentrated on a water bath. The product was extracted in a Soxhlet thimble with methanol and further recrystallised.

In the bleaching experiments imidazole was used as an axial ligand to stabilize the higher valency manganese complex. The stock solution of MnTPP (OAC) (5×10^{-4} M) was prepared in methanol containing 10-fold excess of imidazole, while the solution of MnTPPS (OAC) (5×10^{-4} M) was prepared in distilled water containing excess imidazole. Under these conditions it has been established that OAC is substituted by imidazole in the complex (Renaud *et al* 1985). The activator species are therefore (5, 10, 15, 20 tetraphenyl porphyrinato) manganese(III) imidazole and 5, 10, 15, 20 tetra (*p*-sulphophenyl porphyrinato) manganese(III) imidazole and these will be referred to in the rest of the text as MnTPP(Im) and MnTPPS(Im) respectively.

2.3 Solutions

Methanolic solutions of quinaldine blue and methyl red were used for bleaching experiments. Stock solutions of direct red-81, direct red-23, rhodamine B, rhodamine 6G, eriochrome black T, eriochrome blue black, sunset yellow, tartrazine, methyl orange, carmine MS and carmine AS were prepared in water, while DMF solutions of direct yellow 9, 4-dimethylaminobenzylidene rhodanine and quinaldine red were used. Solutions of sodium perborate (2%), LAS (5.9%), Na_2CO_3 (0.5%) and STP (0.25%) were prepared in water. The reaction was initiated with 2% sodium perborate.

2.4 Measurements

The decay of the substrate concentration was followed by measuring the decrease in optical density at the appropriate absorption maximum of substrates with time on Hewlett-Packard HP 8451 diode array spectrophotometer (figure 2). The reaction mixture contained 0.22% LAS, 0.1% STP, 0.2% Na_2CO_3 , 1.89×10^{-5} M MnTPP(Im) or 2.5×10^{-5} M MnTPPS(Im) and 0.38% sodium perborate. LAS was not present in the experiments carried out in aqueous methanol or DMF. The reaction was initiated by adding 0.05 ml of 2% sodium perborate solution. The same experiment was repeated in the absence of MnTPP(Im). The chromophore concentration was suitably adjusted for measurement of optical density. In aqueous methanolic or aqueous DMF medium the same ingredients have been used with water to solvent ratio 1:0.6 (figure 3).

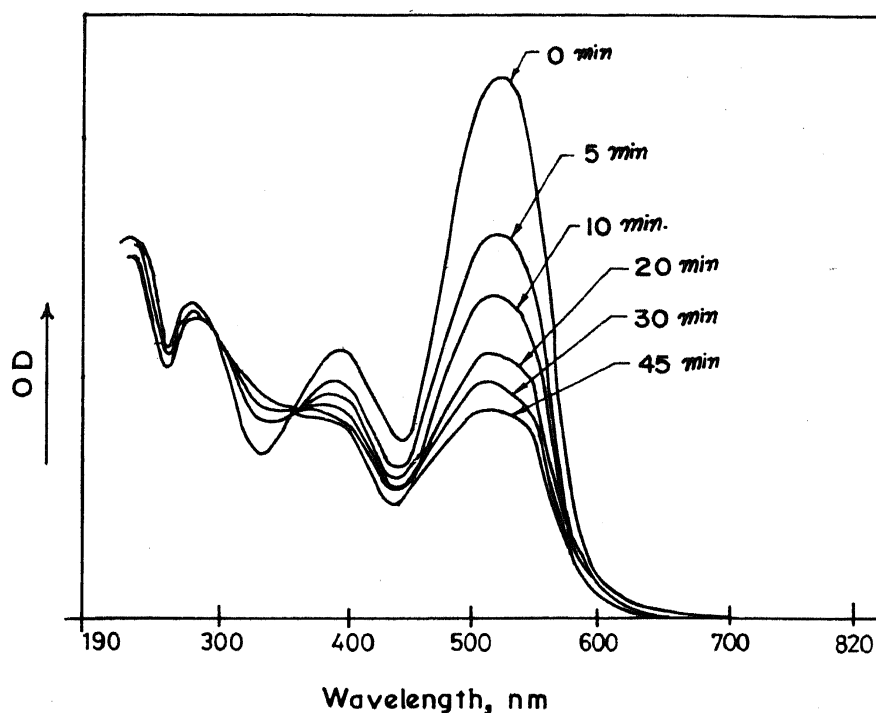


Figure 2. Absorption spectra of reaction mixture containing direct red-81, MnTPP(Im) and perborate at various time intervals in aqueous methanolic medium.

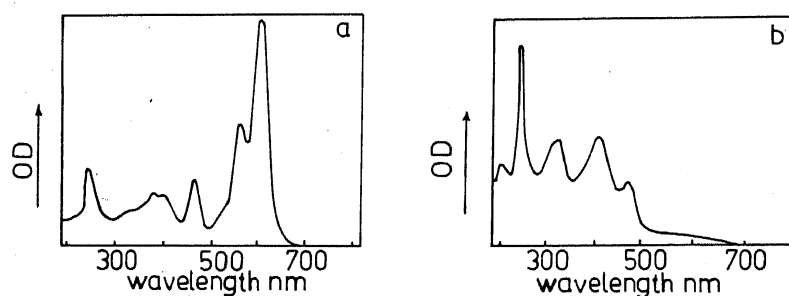


Figure 3. Absorption spectra of reaction mixture at '0' time (a) and after 30 minutes (b) for system containing quinaldine blue, MnTPP(Im) and sodium perborate.

3. Results and discussion

The Soret band of MnTPP(OAC) was observed at 466 nm in methanol and this value is in good agreement with the literature value. The absorption spectrum of MnTPPS(Im) is given in figure 4. The Soret band is at 470 nm and in addition there is a doublet at 380 and 400 nm. The results on the bleaching of 17 substrates with MnTPP(Im) in aqueous methanol, aqueous DMF and aqueous LAS solutions have been presented in table 1. The results on the oxidation of substrates with MnTPPS(Im) are given in table 2. Typical curves giving the absorption spectrum as a function of time for direct red-81 as an example are given in figure 2. Figures 3a and 3b give the absorption spectrum before and after oxidation in the case of quinaldine blue by MnTPP(Im)

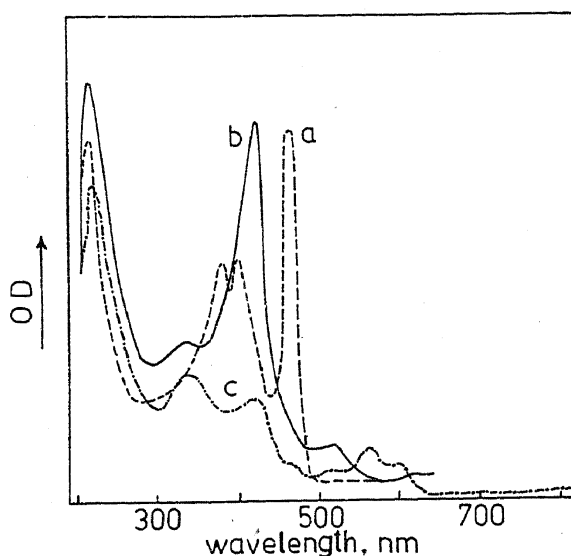


Figure 4. Change in spectral characteristics of MnTPPS(Im): curve 'a' without perborate, curve 'b' 30 seconds after addition of sodium perborate and curve 'c' 5 minutes after addition of perborate.

in aqueous LAS medium. Figure 4 gives the data on the change in spectral characteristics of MnTPPS(Im) mixed with sodium perborate in the absence of substrate. The change in absorbance in the presence and absence of MnTPP(Im) as a function of time at the λ_{max} of the substrate are given in figure 5 in the case of quinaldine blue as an illustrative example of the kinetic course of the reaction.

3.1 Bleaching in aqueous-solvent systems

The absorption spectra as a function of time presented in figure 2 in the case of direct red-81 is indicative of the typical course of reaction. Decrease in absorption at 514 nm, the strong absorption maximum of the dye, and simultaneous increase in absorption at 400 nm, which is suggestive of the formation of a less conjugated product, are clearly seen.

The absorption spectra of the reaction mixture in the case of quinaldine blue before addition of perborate and after the reaction is complete are presented in figure 3 and the results again show the disappearance of the strong maximum and increase in absorption/appearance of new peaks at lower wave lengths again indicating the formation of species with reduced conjugation. There is a decrease in the intensity of the Soret band showing that some of the MnTPP(Im) is also oxidized.

In the absence of the substrate MnTPPS(Im) appears to react readily with perborate (figure 4). At first there is a shift in the absorption maximum from 470 nm to 436 nm and the doublet at 380 and 400 nm disappears (the peak at 400 nm might have merged with the primary maximum). These spectral changes may perhaps be due to the formation of the higher valent manganese complex (as shown in the scheme in figure (6) (Hill and Schardt 1980). However, within 5 minutes MnTPPS(Im) is totally destroyed as perceived by the drastic reduction in intensity of the absorption bands.

It is seen from the results on the oxidation of the substrates by perborate in the absence of MnTPP(Im) in aqueous methanolic solution that as expected quinaldine blue and quinaldine red with olefinic linkage between the aromatic moieties are the

Table 1. Metalloporphyrin catalyzed oxidation of substrates with sodium perborate.

Substrate	Absorption maxima (nm)	Conc. of chromophore (m/dm ³) × 10 ⁴	Percent bleaching after 30 minutes											
			Aq. methanol				Aq. DMF				Aq. LAS			
			Without MnTPP(lm)	With MnTPP(lm)	Without MnTPP(lm)	With MnTPP(lm)	Without MnTPP(lm)	With MnTPP(lm)	Without MnTPP(lm)	With MnTPP(lm)	Without MnTPP(lm)	With MnTPP(lm)	Without MnTPP(lm)	With MnTPP(lm)
Quinaldine blue	606	1.7	90	98	7.6	> 90*	7	98	7.6	> 90*	7	98	7.6	> 90*
Quinaldine red	534	0.75	98.2	48.9	93.6	78.4	6	50.8	93.6	78.4	6	50.8	93.6	78.4
Direct red-23	504	1.51	5	59.7	—	—	0	2	—	—	0	2	—	—
Direct red-81	514	1.51	2	44	—	—	4.6	8.1	—	—	4.6	8.1	—	—
Direct yellow-9	412	1.5	—	—	—	—	1.7	37.8	—	—	1.7	37.8	—	—
Eriochrome blue black	578	6.04	5.9	89.5	3.8	88.5	0	2.2	3.8	88.5	0	2.2	3.8	88.5
Eriochrome black T	652	3.0	0	10.2	6.5	57.5	—	—	6.5	57.5	—	—	6.5	57.5
Carmin MS	528	—	—	—	—	—	5.7	32.4	—	—	5.7	32.4	—	—
Carmin AS	530	—	—	—	—	—	5.7	31.4	—	—	5.7	31.4	—	—
p-Nitrophenylazoresorcinol	452	1.5	0	24.8	0	23.8	8.3	17.4	0	23.8	8.3	17.4	0	23.8
p-Dimethylamine benzylidene rhodanine	460	1.5	—	—	5.4	10.5	5.3	43.6	5.4	10.5	5.3	43.6	5.4	10.5
Methyl orange	462	3.0	8.3	23.8	—	—	4.5	6.8	—	—	4.5	6.8	—	—
Methyl red	428	1.5	3.4	22.9	—	—	0	4.0	—	—	0	4.0	—	—
Sunset yellow	480	3.0	1.7	28.8	—	—	0	1.5	—	—	0	1.5	—	—
Tartrazine	404	0.15	3.3	13.4	0.3	15.8	2.5	0	0.3	15.8	2.5	0	0.3	15.8
Rhodamine B	554	0.35	0.5	2.9	—	—	0	1.6	—	—	0	1.6	—	—
Rhodamine 6G	534	4.5	57.4	49.8	—	—	3.4	4.4	—	—	3.4	4.4	—	—

* Bleaching after few seconds

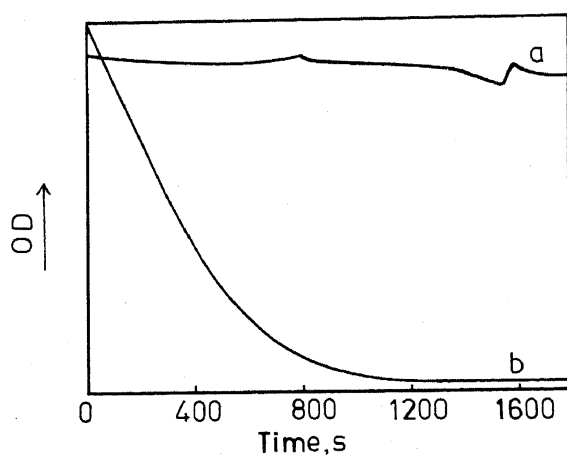
MnTPP 1.89 × 10⁻⁵ MSodium perborate 2.45 × 10⁻³ M

LAS 0.223 %

Table 2. Metalloporphyrin catalysed oxidation of substrates with sodium perborate.

Substrate	Absorption maxima (nm)	Percent bleaching after 30 mins. Aq. LAS solution	
		With MnTPP(Im)	With MnTPPS(Im)
Quinaldine red	534	50.8	13.6
Quinaldine blue	606	98.0	80.6
Direct red-23	504	2.0	5.0
Direct red-81	514	8.1	43.7
Rhodamine 6G	534	4.4	8.0
Rhodamine B	554	1.6	2.7
Tartrazine	404	0.0	18.0
Eriochrome blue black	578	2.2	67.6
Eriochrome black T	652	—	98*
			59.5
			88.2*

* Bleaching after few seconds

**Figure 5.** The change in optical density with time at 606 nm of quinaldine blue, Curve 'a' in the absence of MnTPP(Im) and curve 'b' in the presence of MnTPP(Im).

most susceptible species for bleaching. Rhodamine 6G with quaternary group is also susceptible to bleaching although not to the same extent as the dyes with the olefinic linkage. However, rhodamine B is very resistant to bleaching. This resistance is perhaps due to the additional electron donating alkyl substitution on the quaternary nitrogen thus imparting a stabilizing effect.

The azo dyes appear to be resistant to oxidation by perborate and less than 10% bleaching has been noticed in the case of all the azo dyes examined. Even in the presence of the activator, MnTPP(Im) the azo dyes are bleached only to a limited extent of 25%. The only exception is eriochrome blue black which is bleached in the presence of the catalyst in aqueous methanolic/DMF medium to the extent of 90%. Azo dyes as a class are known for their stability. However, the reasons for the susceptibility of eriochrome blue black to bleaching are not clear. The reactions in

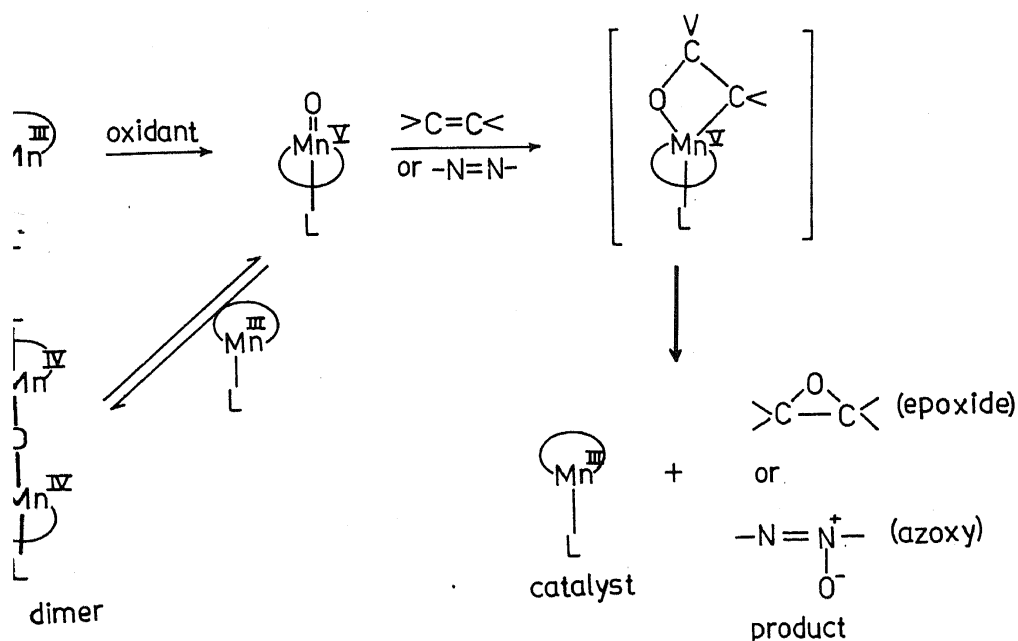


Figure 6. Suggested mechanism for oxidation of substrates by manganese porphyrin complexes.

of this dye also appear to be somewhat complex. The dye is bleached within seconds, but with time the colour is partially regained.

In the case of oxidation in aqueous methanol it is seen from results presented in Table 1 that quinaldine blue, quinaldine red and rhodamine 6G are oxidized by MnTPP(Im) even in the absence of MnTPP(Im). In aqueous DMF quinaldine blue is not oxidized. The reasons for this solvent effect are not very clear. In general, it has been found in the case of most of the dyes studied that the extent of oxidation increases with the concentration of MnTPP(Im), the only exception being rhodamine B. In the presence of a catalyst activator also isolated cases of solvent effect are perceived. Eriochrome black T is found to be more resistant to oxidation in methanolic medium. It has been reported that olefins show higher rates of oxidation in methanolic medium because a high valent oxomanganese species (oxygen transferring) rapidly reacts with substrate (Mannberg *et al* 1986). However, no such general trend was observed in the case of the dyes examined.

On substitution of manganese by cobalt it was found that the catalyzing effect was completely lost. Quinaldine blue, quinaldine red, direct red 81, eriochrome blue black and rhodamine 6G bleached in aqueous DMF by MnTPP(Im) were not at all bleached by CoTPP(Im). The reasons for the ineffectivity of CoTPP(Im) may be due to the lack of formation of high valent oxygen donating species.

Oxidation in micellar systems

The effects on the bleaching of substrate are clearly seen from the results presented in Table 1 and figure 5. Quinaldine blue and red and rhodamine 6G which are bleached rapidly in the absence of the activator in aqueous-solvent system are not bleached in aqueous solutions containing LAS. However, in the presence of MnTPP(Im) the protection is completely lost in the case of quinaldine blue and the substrate

is completely bleached in about 15 minutes (figure 5). In the case of quinaldine red also micellar inhibition is noticed in the absence of MnTPP(Im) but there is no micellar protection in the presence of MnTPP(Im). On the other hand, micellar inhibition of bleaching in the presence of MnTPP(Im) is observed in the case of methyl orange, methyl red, sunset yellow, tartrazine and rhodamine 6G. Only in the case of *p*-dimethylamine benzylidene rhodamine micellar enhancement of bleaching has been observed.

It is well-known that dyes are solubilized by detergent micelles (Mackay 1987). It is conceivable that solubilized dyes residing in the micelles are protected from attack by perborate which resides in the aqueous phase. The reasons for the difference in the behaviour of various dyes are not very clear. The dyes used in these studies are fairly soluble in water. The dyes would thus be distributed between a state of simple aqueous solution and state of solubilization in the surfactant micelles. The resistance to bleaching would depend on the distribution coefficient. In the case of dyes which are not bleached the dye may be present predominantly in the solubilized state.

The soluble activator, MnTPPS(Im) was found to be more effective in the micellar system and some of the substrates which were not bleached by MnTPP(Im) activator were bleached when MnTPPS(Im) was used as the activator. These are clearly seen from the results presented in table 2. The only exception to this trend is quinaldine red.

3.3 Mechanism of bleach activation

The mechanism suggested for the oxidation of olefins by metalloporphyrins is shown in figure 6 (Collman *et al* 1984). The first step in the mechanism is the formation of high valent oxomanganese(V). The decomposition of the active catalyst, manganese(V) occurs via two routes: one with the olefin/chromophore to give epoxide/oxidised species and the second with Mn(III) to form an unreactive μ -oxo dimer. The μ -oxo dimer is catalytically inactive. The oxomanganese species of metalloporphyrin shows blue shift in the Soret band of metalloporphyrin by about 20–40 nm (Grobes *et al* 1980; Schardt *et al* 1982). This type of shift has been observed in the present work in the absence of the substrate.

As shown in figure 4, immediately after addition of sodium perborate the high valent oxomanganese species forms, as indicated by the blue shift. This observation clearly indicates that the bleaching of the substrate is via an oxidized oxomanganese(V) species (figure 6). In the case of olefin oxidation by metalloporphyrin-mediated oxidation with oxygen donors such as hypochlorite, persulphate, peracids, the formation of epoxides has been established (Montanari *et al* 1985; Renaud *et al* 1985). It is likely that oxidation with perborate also results in the formation of epoxides which might undergo further hydrolysis. In the case of azo compounds the formation of the azoxy product during oxidation with molybdenum complexes has been established (Johnson and Gould 1974). It is likely that in the case of azo dyes also the azoxy species is formed. The complete decolouration of eriochrome blue black and quinaldine blue in the dark indicates that the reaction is not light initiated and that the reaction is only taking place by an oxidative mechanism.

4. Conclusions

Perborate oxidative bleaching activated by metalloporphyrin does not appear to be attractive in the context of application in detergent products. Even in the absence of surfactant total bleaching occurs only in the case of quinaldine blue and red with olefinic linkage. Further there is the problem of protection by micellar solubilization by the surfactant. Only quinaldine blue is totally bleached in the presence of LAS. Another complicating factor is the destruction/deactivation of MnTPP(Im) by the oxidant in the absence of the dye. Therefore it is necessary to develop stabler and more powerful catalytic systems in order to have impact in detergent systems.

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