Manganese tetraazaporphines as effective catalysts for the nuclear oxidation of aromatics by peracetic acid

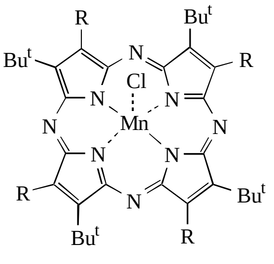
Svetlana V. Barkanova,* Elena A. Makarova, Oleg L. Kaliya and Eugene A. Luk'yanets

Institute of Organic Intermediates and Dyes, 103787 Moscow, Russian Federation. Fax: +7 095 254 1200; e-mail: jerrik@cityline.ru

Manganese tetranitrotetra-*tert*-butyltetraazaporphine at low concentrations (0.02 mol%) effectively catalyses the oxidation of 2-methylnaphthalene by peracetic acid to give 2-methyl-1,4-naphthoquinone in 65% yield with a catalyst turnover number of 3100.

The problem of the nuclear oxidation of non-activated aromatics is noteworthy in terms of both its mechanistic study and practical applications. Thus, 2-methyl-1,4-naphthoquinone (vitamin K_2, menadione, MD) can be produced in moderate yields (~45%) in 2-methylnaphthalene oxidation catalysed by transition metal complexes such as $Re(Me)O_3$ with hydrogen peroxide[1] and water-soluble Mn or Fe tetraphenylporphyrins with $KHSO_5$.[2] Earlier,[3] we have described the oxidation of naphthalene and its methyl derivatives to the corresponding 1,4-quinones (~60% yield) with peracetic acid catalysed by manganese and iron complexes of 3,5-octanitrophthalocyanine. Here, we report the use of a new class of catalysts, manganese complexes of tetraazaporphines (porphyrazines), in particular, Mn^{3+} tetra-R-tetra-*tert*-butyltetraazaporphines (**1**–**3**, Figure 1) in this reaction; we also compared the catalytic activity of these complexes and their carboanalogues, Mn *meso*-tetra(*o*,*o*′-dichloro-*p*-R-phenyl)porphyrins (**4** R = H; **5** R = NO_2). Complexes **2** and **3** [*m*/*z* 892 (M – Me, 100%) and 771 (100%), respectively] were obtained in 91 and 80% yields, respectively, from the corresponding free bases[4] by $Mn(OAc)_3$ treatment (DMFA, 70 °C) followed by chromatography (SiO_2, $CHCl_3$).

In acetonitrile solutions of **1**–**5** both naphthalene and 2-methylnaphthalene are fully and quickly (5–30 min) oxidised with a three-to-five fold excess of peracetic acid (AcOOH, a solution in acetic acid[5]) yielding 1,4-naphthoquinone and menadione, respectively; oligomeric by-products derived from originally formed 1-naphthols were also detected. The reaction product of the oxidation of 2-methylnaphthalene isolated by column chromatography [petroleum ether–benzene (1:1)] is pure menadione (mp 106.3 °C) and does not contain isomeric 6-methyl-1,4-naphthoquinone (HPLC and ^{1}H NMR data), indicating that the described catalytic systems are more selective in menadione production than those reported in refs. 1 and 2, where with a similar isolation procedure the isomeric quinone was obtained in 7 and 58% yields, respectively. Quinone yields[†] determined at the end of the reaction (initial yield, η^{in}) can be significantly enhanced by heating (15 min, 50 °C) the neutralised (Na_2CO_3) reaction mixture (thermal yield, η^{therm}, Table 1). A similar phenomenon was observed earlier[3] in the reactions catalysed by 3,5-octanitrophthalocyanine **6**. It seems that the mechanism of oxidation of the aromatic nucleus includes the formation of a thermally unstable quinone precursor and is common for all the Mn^{3+} porphinoid complexes (PMnX) used here.



1 R = H
2 R = Br
3 R = NO_2

Figure 1 The structure of Mn^{3+} tetra-R-tetra-*tert*-butyltetraazaporphines **1**–**3**.

Table 1 'Initial' and 'thermal' menadione (MD) molar yields[†] in the exhaustive oxidation of 2-methylnaphthalene (0.004 M) with AcOOH (0.016 M) catalysed by **1**–**6**. MeCN + AcOH (~1%, v/v); reaction time, 5–30 min.

Catalyst (Cat) [λ_{max}/nm, ε/dm^3 cm^{-1} mol^{-1} in MeCN]	[Cat]:[2-methylnaphthalene] (mol%)	η^{therm}_{MD} (η^{in}_{MD})^a (mol%)	η^{therm}_{Q} (η^{in}_{Q})^a (mol%)	TN$^b_{MD}$
1 [616, 4.6×10^4]	0.82	25.0 (20)		30.5
1	2.5	29.0 (15)		12
1	5.0	36.0 (7)	16.0 (9.5)	7
2 [634, 3.8×10^4]	0.21	31.5 (3)		150
2	0.41	40.5 (4)		99
2	0.82	46.0 (4)		56
2	1.65	45 (3.5)		27
3^c [620, 3.2×10^4]	0.02	62 (2)	45.0 (5.0)	3100
4	5.0	11 (2)	9.0 (1.0)	2.2
5	2.5	14 (3)		5.6
5	5.0	12 (3)	11.5 (1.5)	2.4
6^d	4.3	55 (20)	51.7 (10.6)	13

^{a}HPLC data (Separon C_{18} reversed phase column; mobile phase, 10–100% aqueous MeCN; λ_{anal}, 250 nm; quinone yields are calculated with an accuracy of 10 rel.%, Q refers to 1,4-naphthoquinone. ^{b}TN$_{MD}$ = [MD]$_{formed}$:[Cat]. ^{c}Fivefold excess of AcOOH. ^{d}From ref. 3.

In our studies of naphthalene oxidation catalysed by **6**[3,6] and of olefin epoxidation catalysed by **1**–**5**,[7–9] we have supposed that two types of highly reactive oxygen-containing complex are generated by the interaction of PMnX with AcOOH: the Mn^V–oxene [PMn^{5+}(O)(L)] and Mn–peroxo [PMn(O_2)(L)] complexes. The latter is thought to play a key role in the oxidation of naphthalene to quinone *via* the formation of intermediate **7**, which in turn produces intermediate **8** by the interaction with PMn^{5+}(O)(L).[‡] Competitive naphthalene and olefin oxidation has revealed[6] that both types of oxygen-containing Mn complexes are generated from the firstly formed molecular 'catalyst–oxidant' complex. Based on these data, Scheme 1 has been proposed for the mechanism of the nuclear oxidation of aromatics in these catalytic systems. Experimental results reported here allow us to detail some stages of this Scheme.[§]

As shown in Figures 2 and 3 and in Table 1, the quinone yield strongly depends on the concentrations of both the catalyst and AcOOH even at full substrate conversion.[¶] The growth of menadione yield with increasing the [AcOOH]:[2-methylnaphthalene] ratio up to 5:1 (higher than it is necessary for

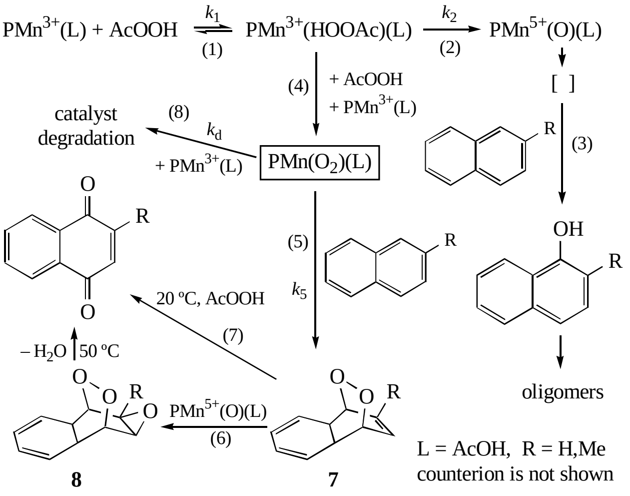
---

[†] Molar yield values were calculated as [product]$_{formed}$/[substrate]$_{reacted}$. At exhaustive substrate oxidation, [substrate]$_{reacted}$ = [substrate]$_0$.

[‡] The indirect proof of the structure of intermediate **8** as reported earlier;[3,6] additional data for the affirmation of the structure of **8** will be published later.

[§] The rate of the reaction catalysed by **3** is too high to be measured by common methods. Assuming that the sum of 'oxenoid' and 'peroxide' pathways describes all possible transformations of aromatic molecules in the reaction studied, the menadione yield may be considered to be proportional to the rate of menadione formation.

[¶] Catalysts **1** and **4** at low content (< 0.1 mol%) do not produce quinones; exhaustive naphthalene oxidation by AcOOH leads in these cases to oxygen-containing oligomers derived from originally formed 1-naphthol.



$$\frac{\eta_{\mathrm{Q}}^{\mathrm{therm}}}{100-\eta_{\mathrm{Q}}^{\mathrm{therm}}} \sim \frac{W_{\mathrm{Q}}}{W_{\mathrm{NfOH}}} \sim \frac{[\mathrm{PMnL}]_0[\mathrm{AcOOH}]_0[\mathrm{R\text{-}naphtalene}]_0}{k_5[\mathrm{R\text{-}naphthalene}]_0 + k_{\mathrm{d}}[\mathrm{PMnL}]_0} \qquad (1)$$

quinone formation, 3:1)[††] together with the relationship shown in Figure 2 (curve *1*) evidence the participation of second molecules of both AcOOH and the catalyst in the quinone formation at the rate-determining step (or before it), *i.e.*, at macro stage (4). It seems that the reaction of the molecular complex PMn(AcOOH)(L) with the second AcOOH molecule followed by the formation of a Mn peroxo complex is catalysed by PMnX. The dependence of $\eta_{\mathrm{MD}}^{\mathrm{in}}$ on catalyst concentration (Table 1; Figure 2, curve *2*) agrees with the hypothesis on the participation of Mn^{5+}–oxene in quinone formation at stage (6), which we have proposed earlier[6] in competitive naphthalene and olefin oxidation catalysed by **6**.[6] Indeed, according to Scheme 1, as the catalyst content was increased, the contribution of stage (7) to the overall transformations of intermediate **7** diminishes because of an increase in the stationary concentration of Mn–oxene, which in turn leads to a decrease in the $\eta_{\mathrm{MD}}^{\mathrm{in}}$ value. At high catalyst contents (> 0.02 mol% for **3**; Figure 2, curve *1*) the promotion of reaction (4) with catalyst concentration may be lowered by a competitive reaction of catalyst degradation with the Mn peroxo complex (8). Equation (1) for the relative share of menadione formation calculated from Scheme 1 is in qualitative agreement with the experimental data presented here and reported earlier.

For Mn complexes of porphyrins and tetraazaporphines, we have shown[8,9] that the transformation of molecular complex to Mn–oxene(s) [reaction (2)] is enhanced by electronegative substitution in the porphinoid macrocycle. The data described here allow us to conclude that electron-withdrawing substituents stimulate the formation of Mn peroxo complexes even more: for **1**–**3**, the maximum value of the yield of menadione (and hence the contribution of the 'peroxide' pathway) increases in the order **1** > **2** > **3** (25, 45 and 65%, respectively). This means that in the azaporphine molecule, the 'peroxide' pathway is more sensitive to electronegative peripheral substitution than the 'oxenoid' one. It is noteworthy that Mn porphyrins **4** and **5** exhibit slight efficiency in menadione production and provide very low turnover numbers; the reason for the different reactivity of Mn^{3+} porphyrins and azaporphines in the production of *para*-quinone is now under study.

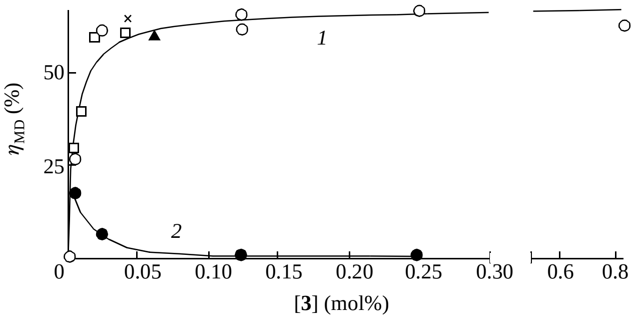


Figure 2 The dependencies of 'thermal' (*1*) and 'initial' (*2*) menadione yields on the concentration of **3** at full substrate conversion. [AcOOH]: [2-methylnaphthalene] = 5:1. [2-methylnaphthalene]: (○) 0.004, (▲) 0.008, (□) 0.024 and (×) 0.05 M. (At [**3**] = 0.005 mol% the substrate conversion was 75%, and the menadione yields were calculated on the reacted 2-methylnaphthalene.)

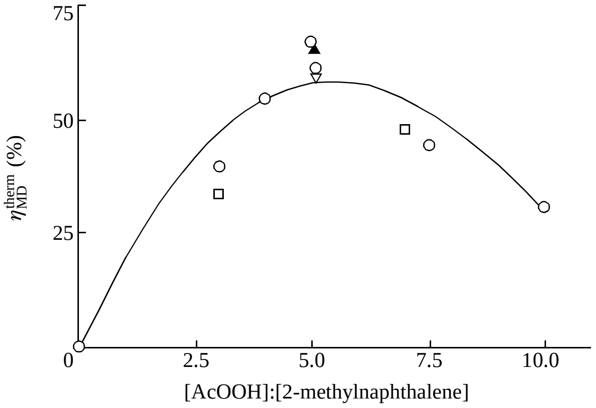


Figure 3 The dependence of the 'thermal' menadione yield on the oxidant excess. [**3**] = 0.02–0.1 mol%, [2-methylnaphthalene]: (○) 0.004, (▽) 0.008, (□) 0.024 and (▲) 0.05 M.

Thus, within the group of Mn porphinoids studied here, Mn tetraazaporphine **3** was found to be the most effective catalyst in the production of *para*-quinone from non-activated (or slightly activated) aromatics not only due to the well-known effect of catalyst stabilization by electronegative peripheral substitution, but also due to the highest reactivity in the formation of the Mn peroxo complex. This catalyst at low content (≤ 0.02 mol%) produces a yield of 60–65% menadione in the oxidation of 2-methylnaphthalene with an extremely high catalyst turnover number (3100).

This work was supported by the Russian Foundation for Basic Research (grant no. 97-03-32327). We are grateful to Professor S. Banfi and L. Pozzi (University of Milan) for the provision of samples of compounds **4** and **5**.

References

1 W. Adam, W. A. Herrmann, J. Lin, C. R. Saha-Mëller, R. W. Fischer and J. D. G. Correia, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2475.
2 R. Song, A. Sorokin, J. Bernadou and B. Meunier, *J. Org. Chem.*, 1997, **62**, 673.
3 S. V. Barkanova, V. M. Derkacheva, O. V. Dolotova, V. D. Li, V. M. Negrimovski, O. L. Kaliya and E. A. Luk'yanets, *Tetrahedron Lett.*, 1996, **37**, 1637.
4 (*a*) V. N. Kopranenkov, I. D. Mundshtukova and E. A. Luk'yanets, *Khim. Geterotsikl. Soedin.*, 1994, 30 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1994, 26]; (*b*) E. A. Makarova, V. N. Kopranenkov and E. A. Luk'yanets, *Khim. Geterotsikl. Soedin.*, 1994, 1206 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1994, 1043].
5 S. Banfi, F. Montanari, S. Quici, S. V. Barkanova, O. L. Kaliya, V. N. Kopranenkov and E. A. Luk'yanets, *Tetrahedron Lett.*, 1995, **36**, 2317.
6 S. V. Barkanova and O. L. Kaliya, *J. Porph. Phthal.*, 1999, 180.
7 S. Banfi, F. Montanari, S. V. Barkanova and O. L. Kaliya, *J. Chem. Soc., Perkin Trans. 2*, 1997, **8**, 1577.
8 S. Banfi, L. Pozzi, S. Quici, S. V. Barkanova and O. L. Kaliya, *J. Chem. Soc., Perkin Trans. 2*, in press.
9 S. V. Barkanova, E. A. Makarova, O. L. Kaliya and E. A. Luk'yanets, *J. Chem. Soc., Perkin Trans. 2*, submitted.

Received: 25th May 1999; Com. 99/1491

[††] The decrease of menadione yield at [AcOOH]:[2-methylnaphthalene] > > 5:1 can be explained by competitive radical decomposition of excess AcOOH followed by 2-methylnaphthalene oxidation with the radicals formed without menadione formation.