Kinetic studies on the interactions of manganese–porphyrins with peracetic acid. Part 1. Epoxidation of alkenes and hydroxylation of aromatic rings

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Stefano Banfi,*[a]† **Marco Cavazzini,**[a] **Gianluca Pozzi,**[a] **Svetlana V. Barkanova***[b] **and Oleg L. Kaliya**[b]

[a] *Dipartimento di Chimica Organica e Industriale e Centro CNR Studio per la Sintesi e Stereochimica di Speciali Sistemi Organici, Via C. Golgi 19, 20135 Milano, Italy*
[b] *Organic Intermediates and Dyes Institute, B. Sadovaya 1/4, 103787 Moscow, Russia*

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The mechanism of peracetic acid interactions with Mn^{III} complexes of *meso*-tetra(2,6-dichloro-4-R-phenyl)-porphyrins (RTDCPPMnCl; R = CH_3O, H, Br, Cl or NO_2) in acetonitrile–acetic acid has been studied. Analysis of the kinetic data revealed that both in *cis*-stilbene epoxidation and naphthalene hydroxylation the first step of the reaction is the reversible formation of an intermediate adduct '**A**' between the catalyst and the oxidant. The subsequent irreversible transformation of '**A**' with rate constant k_2 leads to the formation of two high-valent oxometallo species, [RTDCPPMn^{V}(O)] and supposedly [RTDCPPMn^{IV}(O)]$^{+\bullet}$. These species are in equilibrium and show distinct oxidation abilities towards the substrates.

Introduction

Biomimetic oxidations catalysed by metal complexes of synthetic porphyrins (PorM) have been widely studied for almost twenty years.[1,2] It is now generally accepted that these reactions occur with the participation of high-valent oxometallo species which can be generated by the interaction of PorM with oxygen donors such as hydrogen peroxide,[3] hydroperoxides,[4,5] iodosylarenes,[6] sodium hypochlorite,[7,8] potassium monopersulfate,[9] amine *N*-oxides,[10] peracids[11,12] and others. Most studies have been devoted to the use of iron (PorFe^{III}) and manganese (PorMn^{III}) porphyrin complexes in olefin epoxidations, for which such complexes exhibit very high catalytic activities. Theoretical predictions[13] as well as experimental probes[14] evidenced that epoxides are formed through a concerted mechanism of oxygen atom transfer from the high-valent oxometallo species to the carbon–carbon double bond. In the case of PorFe^{III}, this species is believed to be an oxoiron(IV)–porphyrin π-radical cation [PorFe^{IV}(O)]$^{+\bullet}$.[15] The intervention of several intermediates, namely oxomanganese(IV)–porphyrin, PorMn^{IV}(O),[16] oxomanganese(IV)–porphyrin π-radical cation, [PorMn^{IV}(O)]$^{+\bullet}$,[3,17] and an elusive oxomanganese(V)–porphyrin, PorMn^{V}(O),[18] has been postulated for PorMn^{III} catalysed oxidations. Each of these species seems to have a specific reactivity towards different substrates. For instance, PorMn^{IV}(O) slowly oxidizes olefins through a one-electron oxidation mechanism producing epoxides in low yields,[16] while PorMn^{V}(O) is able to transfer a single oxygen atom to olefins with very high reaction rates and selectivities.[18] On the other hand, [PorMn^{IV}(O)]$^{+\bullet}$ can participate in two-electron or one-electron oxidation reactions, the former being largely favoured.[3] These high-valent oxomanganese species are convertible into each other and their stationary concentrations in solution strongly depend on the reaction conditions, in particular on the pH of the media and on the presence and the nature of axial ligands or counter anions. It was recently established that the first oxometallo species produced by the reaction of Mn^{III} *meso*-tetra(*N*-methylpyridinio)porphyrin with *m*-chloroperbenzoic acid, HSO_5^- or ClO^- is a highly reactive PorMn^{V}(O) species which quickly converts into its reduced form [PorMn^{IV}(O)].[18] In the reaction of H_2O_2 with Mn^{III} *meso*-tetra(2,6-dimethyl-3-sulfonatophenyl)porphyrin the ratio of these two species has been shown to be dependent both on the pH of the reaction media and on the nature of the axial ligand.[3] Nevertheless, mechanism studies of oxidation reactions catalysed by PorMn^{III} complexes usually disregard the possible contemporary presence of at least three types of active oxomanganese species featuring specific reactivity.

Another relevant mechanistic point concerns the reversible formation of "catalyst–oxidant" molecular adducts prior to generation of the high-valent oxometallo species. In the case of PorFe^{III} and PorMn^{III} catalysed oxidations with hydrogen peroxide,[3] alkyl hydroperoxides[19] and amine *N*-oxides[10] the presence of such intermediates has been demonstrated by kinetic studies. Molecular adducts between PorM and NaOCl or iodosylbenzene have also been suggested.[20,21] The situation is more complicated for oxidation reactions carried out in the presence of peracids, since these oxidants can react with PorM to give peroxometallo species PorMOOCOR. Formation of [PorFe^{IV}(O)]$^{+\bullet}$ from PorFeOOCOAr during PorFe^{III} catalysed oxidation reactions with perbenzoic acids has been postulated,[22] by analogy with the behaviour of PorMnOOCOAr which are well-known as precursors of high-valent oxomanganese complexes.[23] It has also been demonstrated that $PorFeOOCOCH_3$ and $PorMnOOCOCH_3$ (PorMnOOAc) directly oxidize alkenes.[23,24] However, the incidence of oxygen transfer from these reactive intermediates to the substrate becomes noticeable only when reaction conditions do not allow their conversion into the corresponding high-valent oxometallo species. We have recently found that the Mn^{III} complexes of *meso*-tetra(2,6-dichlorophenyl)porphyrin and *meso*-tetra-(2,6-dichloro-4-nitrophenyl)porphyrin, as well as those of tetra-*tert*-butyltetraazaporphine and octanitrophthalocyanine, catalyse the quantitative, stereoselective epoxidation of alkenes with peracetic acid (AcOOH) in acetonitrile/acetic acid.[14] The

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† Present address: Dipartimento di Biologia Strutturale e Funzionale, Università dell'Insurbia, Via Dunant 3, 21100 Varese, Italy.

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Table 1 Reagent concentrations and experimental rate constant values for *cis*-stilbene (cSt) and naphthalene (Nph) oxidation with peracetic acid catalysed by RTDCPPMn-Cl **1**–**5** at 20 °C[a]

Catalyst	[Catalyst]$_0$/mol dm^{-3}	[cSt]$_0$/mol dm^{-3}	[Nph]$_0$/mol dm^{-3}	[AcOOH]$_0$[b,c]/mol dm^{-3}	k_{ol}[d]/s^{-1}	k_{Nph}[d]/s^{-1}	K_1[e]/M^{-1}
1	$(0.2–6.7) \times 10^{-5}$	1.0×10^{-2}	$(1.25–2.5) \times 10^{-2}$	$(0.62–5.0) \times 10^{-2}$	1.0	0.51	65[f]
2	$(0.9–15) \times 10^{-6}$	$(0.5–1.0) \times 10^{-2}$	$(0.4–1.25) \times 10^{-2}$	$(0.62–10) \times 10^{-2}$	0.85	0.38	63[f]
3	$(2.1–9.0) \times 10^{-6}$	$(0.5–1.0) \times 10^{-2}$	1.25×10^{-2}	$(0.73–4.5) \times 10^{-2}$	1.8	0.94	69[f]
4	$(2.0–7.0) \times 10^{-6}$	1.0×10^{-2}	1.25×10^{-2}	$(0.62–5.0) \times 10^{-2}$	2.0	0.85	60[f]
5	$(0.33–6.7) \times 10^{-6}$	$(1.0–2.0) \times 10^{-2}$	$(1.25–2.5) \times 10^{-2}$	$(0.62–10) \times 10^{-2}$	4.3	3.65	64[f] 51[g]

[a] Reaction conditions: see Experimental section; several measurements were done within the shown concentration ranges. [b] At high [AcOOH]$_0$ competitive radical AcOOH decomposition leads to non-selective *cis*-stilbene oxidation. [c] AcOH is present in AcOOH solutions ([AcOH]$_{ox} \approx$ 10[AcOOH]$_0$). Some experiments (see Fig. 1) were done at [AcOH]$_0$ = const. = [AcOH]$_{ox}$ + [AcOH]$_{add}$. [d] Experimental error = ±10%. [e] Estimated with accuracy = ±30%. [f] Determined in *cis*-stilbene epoxidation. [g] Determined in naphthalene hydroxylation.

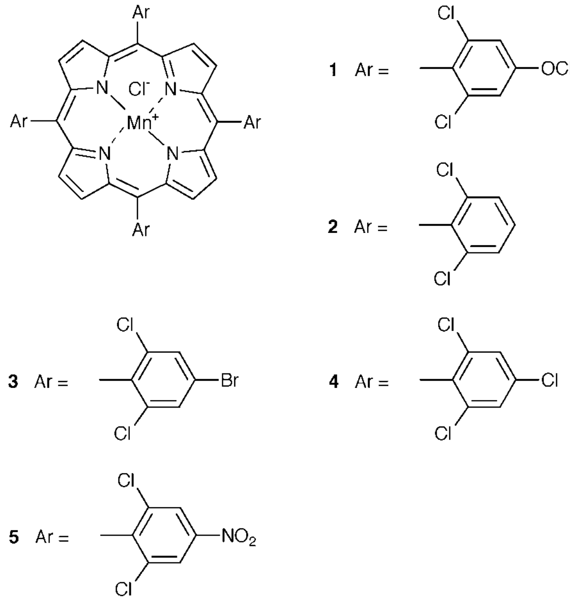


Fig. 1

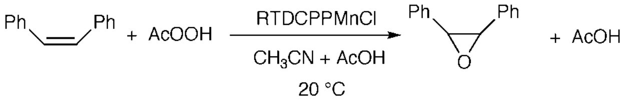
high selectivity of this reaction led us to reject the possibility that PorMn^{IV}(O) or PorMnOOAc were the active catalytic species and to assume that only PorMn^{V}(O) species were involved in the oxygen transfer to the substrate. Subsequent kinetic studies of *cis*-stilbene epoxidation and 1,1-diphenyl-2-picrylhydrazine one-electron oxidation pointed to the reversible formation of an intermediate adduct '**A**' between the catalyst and the oxidant as the first step for both reactions. Adduct '**A**' would then generate PorMn^{V}(O) in an irreversible stage.[25] Unfortunately, these preliminary investigations elucidated neither the exact nature of the first intermediate '**A**', which could be a molecular complex [PorMn–AcOOH](X) or the corresponding peracetate PorMnOOAc, nor the possible role of high-valent oxomanganese species other than PorMn^{V}(O). A better understanding of these issues is crucial for estimating the rate constants of the elementary reaction steps. Indeed, in our catalytic system overall epoxidation rates are independent of the nature of the substrate at a given PorMn^{III} concentration and are determined by the rate of formation of the catalytically active species, in agreement with a concerted mechanism of oxygen transfer.[25] The comparison of rate constant values for the formation of, supposedly, PorMn^{V}(O) from different PorMn^{III} should help to establish significant catalyst structure/activity relationship. A related approach has been followed by Groves and Watanabe for PorFe^{III} catalysed oxidations in the presence of perbenzoic acids.[22,26] They found that electron-donor substituents on the porphyrin ring increase the rate constant values for the transformation of PorFeOOCOAr into [PorFe^{IV}(O)]$^{+\bullet}$.[26] With many oxidants, the catalytic efficiency and the chemical stability of PorMn^{III} usually follow an opposite trend.[27] However, the structure/activity relationship for PorMn^{III} catalysed oxidations in the presence of peracids has not been explored yet.

We have now studied the kinetics of four different oxidation reactions catalysed by Mn^{III} *meso*-tetra(2,6-dichloro-4-R-phenyl)porphyrins (RTDCPPMnCl, **1**–**5**, Fig. 1) in the presence of peracetic acid. The results obtained in *cis*-stilbene (cSt) epoxidation to *cis*-stilbene epoxide (cStO) and naphthalene (Nph) hydroxylation to naphthols (NphOH) are reported here. The one-electron oxidation of 1,1-diphenyl-2-picrylhydrazine (DPPH) and Zn tetra-4-*tert*-butylphthalocyanine (PcZn) to the corresponding stable radical (DPP$^\bullet$) and the π-radical cation [(PcZn)$^{+\bullet}$][28] respectively will be discussed in the following paper.[29]

Results and discussion

Kinetics of *cis*-stilbene epoxidation

Epoxidation of *cis*-stilbene to *cis*-stilbene epoxide catalysed by Mn-porphyrins **1**–**5** (Scheme 1) was carried out in acetonitrile in the presence of solutions of peracetic acid in acetic acid (see Experimental section). Reagent concentrations are indicated in Table 1. With all catalysts the rate of *cis*-stilbene disappearance (W_{ol}^{obs}, "ol" = olefin) was found to be independent of [*cis*-stilbene]$_0$ at [*cis*-stilbene]$_0$ > 0.005 M and first order in [RTDCPPMnCl]$_0$. Furthermore, W_{ol}^{obs} is equal to the rate of *cis*-stilbene epoxide formation (W_{ep}^{obs}, "ep" = epoxide) and it exhibits a Michaelis–Menten type dependence on [AcOOH]$_0$, as shown for catalyst **2** in Fig. 2.



Scheme 1

As shown in Fig. 3 for catalyst **1**, the rate of *cis*-stilbene disappearance is of zero order with respect to [*cis*-stilbene]$_\tau$, where τ is the reaction time. Independence of $W_{ol(ep)}^{obs}$ on both [*cis*-stilbene]$_0$ and [*cis*-stilbene]$_\tau$, together with its dependence on [AcOOH]$_0$, indicates that the alkene acts as a trap for an oxidizing species formed in an *irreversible* stage from an intermediate '**A**', which is the product of *reversible* interactions of RTDCPPMnCl with AcOOH. This means that, under the conditions used (*i.e.* large excess of substrate with respect to the catalyst), the rate limiting step is the conversion of the intermediate into the high-valent oxomanganese–porphyrin.

The experimentally determined reaction rates $W_{ol(ep)}^{obs}$ are fitted well by the kinetic expressions (1) and (1a), where K_1 is the equilibrium constant for the reversible step. The values of K_1 for the five Mn-porphyrins studied (Table 1), estimated according to eqn. (1) from the dependence of $W_{ol(ep)}^{obs}$ on [AcOOH]$_0$

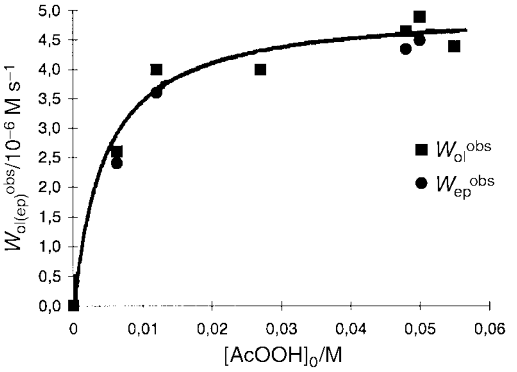


Fig. 2 Dependence of the rates of *cis*-stilbene disappearance ($W_{\mathrm{ol}}{}^{\mathrm{obs}}$) and *cis*-stilbene epoxide formation ($W_{\mathrm{ep}}{}^{\mathrm{obs}}$) on $[\mathrm{AcOOH}]_0$ for *cis*-stilbene epoxidation catalysed by PorMn **2**. $[\mathbf{2}]_0 = 5 \times 10^{-6}$ M, $[cis\text{-stilbene}]_0 = 0.01$ M; $[\mathrm{AcOH}]_0 = [\mathrm{AcOH}]_{\mathrm{ox}} + [\mathrm{AcOH}]_{\mathrm{add}} = 0.5$ M.

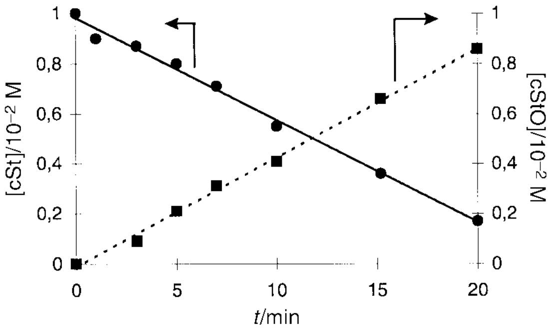


Fig. 3 Kinetic curves of *cis*-stilbene (cSt) disappearance and *cis*-stilbene epoxide (cStO) formation for PorMn **1** catalysed *cis*-stilbene epoxidation with AcOOH. $[\mathbf{1}]_0 = 1 \times 10^{-5}$ M, $[\mathrm{AcOOH}]_0 = 0.0125$ M, $[\mathrm{AcOH}]_{\mathrm{ox}} = 0.17$ M.

$$W_{\mathrm{ol(ep)}}{}^{\mathrm{obs}} = \frac{k_{\mathrm{ol(ep)}}K_1[\mathrm{RTDCPPMnX}]_0[\mathrm{AcOOH}]_0}{1 + K_1[\mathrm{AcOOH}]_0} \qquad (1)$$

$$W_{\mathrm{ol(ep)}}{}^{\mathrm{obs}} = k_{\mathrm{ol(ep)}}[\mathrm{RTDCPPMnX}]_0 \quad (\text{at } K_1[\mathrm{AcOOH}]_0 > 1) \qquad (1\mathrm{a})$$

(Fig. 2), are similar. Therefore K_1 is not influenced by the nature of the substituents placed on the phenyl rings of tetraarylporphyrin. The experimental rate constant values k_{ol} reported in Table 1 were calculated from eqn. (1a) at $[\mathrm{AcOOH}]_0 > 0.025$ M, the oxidant concentration above which $W_{\mathrm{ol(ep)}}{}^{\mathrm{obs}}$ is independent of $[\mathrm{AcOOH}]_0$. These values are also independent of acetic acid concentration at $[\mathrm{AcOH}]_0 > 0.06$ M.

The simplest reaction mechanism explaining the experimental findings is outlined in Scheme 2. This mechanistic

$$\mathrm{RTDCPPMnX} + \mathrm{AcOOH} \overset{K_1}{\rightleftharpoons} \mathbf{A}$$

$$\mathbf{A} \xrightarrow{k_2} \mathrm{RTDCPPMn^{V}(O)(X)} + \mathrm{AcOH}$$

$$\mathrm{RTDCPPMn^{V}(O)(X)} + \mathrm{cSt} \xrightarrow{k_3} \mathrm{RTDCPPMnX} + \mathrm{cStO}$$

Scheme 2

approach implies that $\mathrm{RTDCPPMn^{V}(O)(X)}$ is the only product of the transformation of intermediate '**A**', *i.e.* that other

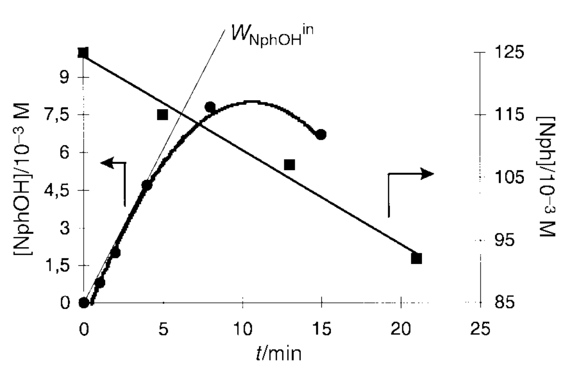


Fig. 4 Kinetic curves of naphthalene (Nph) disappearance and naphthol (NphOH) formation for PorMn **5** catalysed naphthalene oxidation with AcOOH. $[\mathbf{5}]_0 = 6.7 \times 10^{-7}$ M, $[\mathrm{Nph}]_0 = 0.0125$ M, $[\mathrm{AcOOH}]_0 = 0.024$ M, $[\mathrm{AcOH}]_{\mathrm{ox}} = 0.28$ M. ($[\mathrm{NphOH}] = [\text{1-NphOH}] + [\text{2-NphOH}]$).

high-valent oxomanganese species ($\mathrm{RTDCPPMn^{IV}(O)(X)}$ or $[\mathrm{RTDCPPMn^{IV}(O)}]^{+\bullet}(\mathrm{X})$) are absent in the studied reaction. However, in the present catalytic system the rates of alkene epoxidation do not depend on the nature of the substrate: the rates of *cis*- and *trans*-stilbene and of 1-dodecene epoxidation were found to be comparable, thus indicating that the alkene in excess acts as a trap for the same oxidizing species and is oxidized *after* the rate-limiting step.[25] As a consequence, epoxidation of alkenes is not advisable for detecting the possible contemporary presence of different high-valent oxomanganese species featuring slightly different oxidizing properties. In order to gain more insights we decided to study the kinetics of naphthalene (Nph) monooxygenation. We have recently shown that Mn-porphyrin **5** catalyses naphthalene hydroxylation to a mixture of 1- and 2-naphthols (9 : 1, NphOH) under the reaction conditions reported here for *cis*-stilbene epoxidation.[30] If these two reactions involve the same oxidizing species the rates of disappearance of *cis*-stilbene and naphthalene, as well as the rates of epoxide and naphthol formation, should be equal.

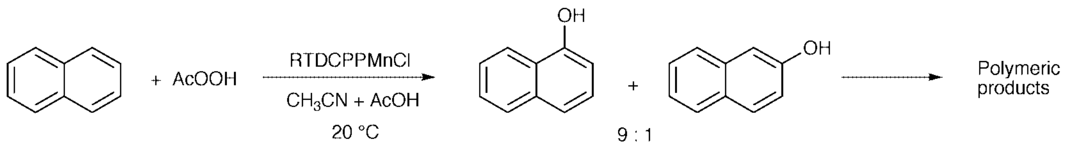
Kinetics of naphthalene hydroxylation

Catalytic hydroxylation of naphthalene (Scheme 3) to NphOH as primary products was carried out at the reagent concentrations reported in Table 1. The rate of naphthalene disappearance ($W_{\mathrm{Nph}}{}^{\mathrm{obs}}$) for Mn-porphyrin **1**–**5** catalysed reactions was equal to the initial rate of NphOH (1-naphthol plus 2-naphthol) formation ($W_{\mathrm{NphOH}}{}^{\mathrm{in}}$) (Fig. 4).‡ Analogously to *cis*-stilbene epoxidation, experimentally found kinetic expressions for $W_{\mathrm{Nph}}{}^{\mathrm{obs}}$ and $W_{\mathrm{NphOH}}{}^{\mathrm{in}}$ [eqns. (2) and (2a)] were

$$W_{\mathrm{Nph(NphOH)}}{}^{\mathrm{obs}} = \frac{k_{\mathrm{Nph(NphOH)}}K_1[\mathrm{RTDCPPMnX}]_0[\mathrm{AcOOH}]_0}{1 + K_1[\mathrm{AcOOH}]_0} \qquad (2)$$

$$W_{\mathrm{Nph(NphOH)}}{}^{\mathrm{obs}} = k_{\mathrm{Nph(NphOH)}}[\mathrm{RTDCPPMnX}]_0 \quad (\text{at } K_1[\mathrm{AcOOH}]_0 > 1) \qquad (2\mathrm{a})$$

first order in $[\mathrm{RTDCPPMnCl}]_0$, exhibited a Michaelis–Menten type dependence on $[\mathrm{AcOOH}]_0$ (Fig. 5) and were independent



Scheme 3

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‡ Further oxidation of NphOH gives unidentified polymeric products.

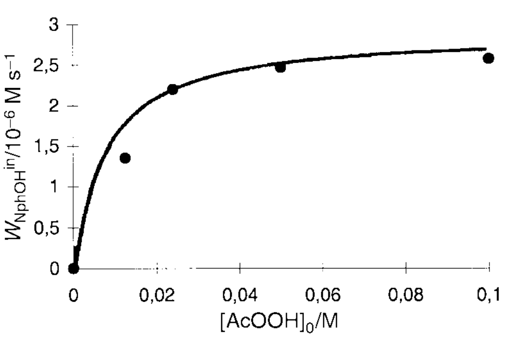

Fig. 5 Dependence of the initial rate of naphthol formation (W_{NphOH}^{in}) on $[AcOOH]_0$ in naphthalene (Nph) oxidation with peracetic acid catalysed by PorMn **5**. $[\mathbf{5}]_0 = 6.7 \times 10^{-7}$ M, $[Nph]_0 = 0.0125$ M, $[AcOH]_{ox} = 0.3$ M.

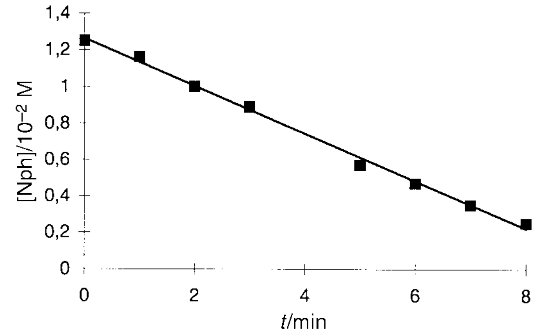

Fig. 6 Kinetic curve of naphthalene (Nph) disappearance for PorMn **5** catalysed oxidation with AcOOH. $[\mathbf{5}]_0 = 6.7 \times 10^{-6}$ M, $[AcOOH]_0 = 0.025$ M, $[AcOH]_{ox} = 0.3$ M.

both of $[naphthalene]_0$ (at $[naphthalene]_0 > 0.004$ M) and, for the most stable catalyst **5**,§ $[naphthalene]_\tau$ (Fig. 6).

The comparison of W_{Nph}^{obs} and W_{ol}^{obs} obtained with the five catalysts showed that the rates of epoxidation and hydroxylation become independent of $[AcOOH]_0$ at $[AcOOH]_0 > 0.025$ M as found in the epoxidation of *cis*-stilbene. Accordingly, the equilibrium constant K_1 for catalyst **5** estimated from eqn. (2) and the dependence of W_{NphOH}^{in} shown in Fig. 5 are close to those found in the oxidation of *cis*-stilbene. This indicates the reversible formation of a common intermediate '**A**' in both reactions.

Independence of W_{Nph}^{obs} of naphthalene concentration confirms that naphthalene acts as a trap of high-valent oxomanganese species. However, k_{Nph} calculated from eqn. (2a) at $[AcOOH]_0 > 0.025$ M (Table 1) are generally lower than the corresponding k_{ol} values ($k_{Nph} < k_{ol}/2$). Such data strongly support the involvement of two different high-valent oxomanganese species in alkene epoxidation and naphthalene hydroxylation, similar to what was found in an investigation on the competitive oxidation of naphthalene and 1,7-octadiene catalysed by Mn^{III} octanitrophthalocyanine.[29] In order to confirm this hypothesis, competitive experiments of *cis*-stilbene and naphthalene oxidation with AcOOH in the presence of **2** were carried out.

Competitive oxidation of *cis*-stilbene and naphthalene in the presence of catalyst 2

As shown in Figs. 7 and 8, the addition of naphthalene led to a decrease in *cis*-stilbene oxidation rate and *vice versa*. In the hydroxylation of naphthalene the addition of *cis*-stilbene lowered both the formation rate of 1-naphthol and the disappearance rate of the substrate to the same extent. For instance, at $[\mathbf{2}]_0 = 0.27 \times 10^{-5}$ M, $[naphthalene]_0 = 0.004$ M, $[AcOOH]_0 = 0.0125$ M, the addition of 0.005 M *cis*-stilbene decreased W_{Nph}^{obs} and W_{NphOH}^{in} by 2.9 and 2.2 times, respectively.

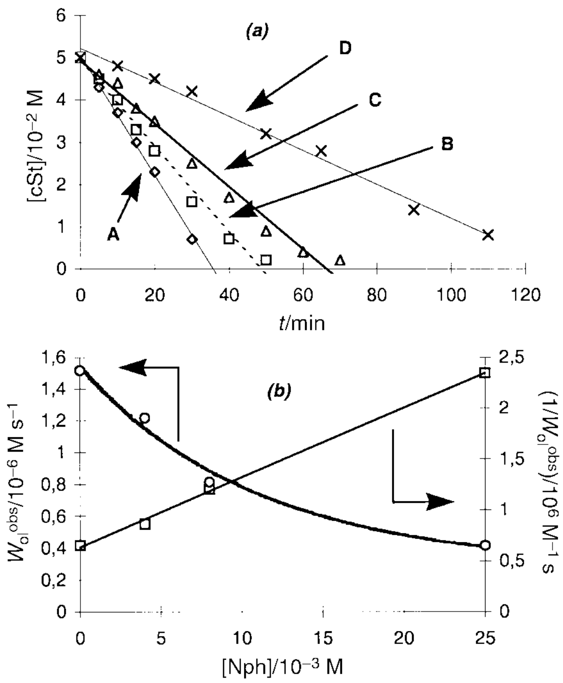

Fig. 7 (*a*) Dependence of the rate of *cis*-stilbene (cSt) disappearance on the concentration of added naphthalene (Nph) in competitive experiments. $[AcOOH]_0 = 0.05$ M, $[\mathbf{2}]_0 = 2.7 \times 10^{-6}$ M. $[Nph]_{add}$: A, 0; B, 4×10^{-3}; C, 8×10^{-3}; D, 25×10^{-3} M. (*b*) Dependence of *cis*-stilbene oxidation rate (W_{ol}^{obs}) on $[Nph]_{add}$ and its linearization.

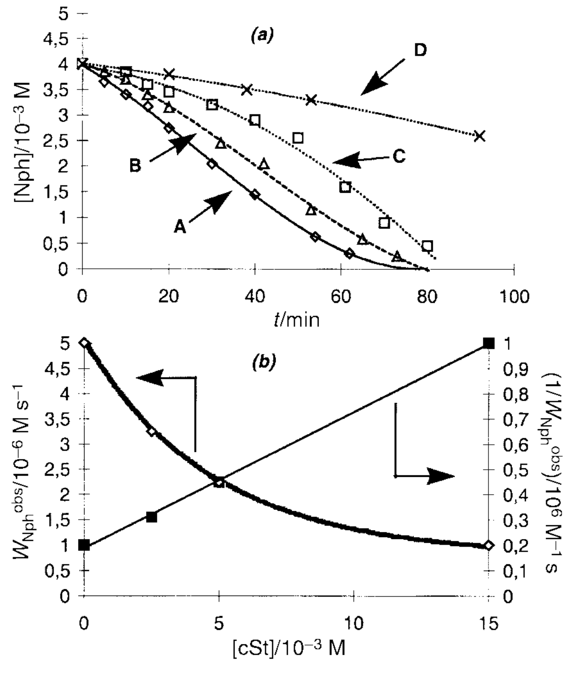

Fig. 8 (*a*) Dependence of the rate of naphthalene (Nph) disappearance on the concentration of added *cis*-stilbene (cSt) in competitive experiments. $[AcOOH]_0 = 0.05$ M, $[\mathbf{2}]_0 = 2.7 \times 10^{-6}$ M. $[cSt]_{add}$: A, 0; B, 2.5×10^{-3}; C, 5×10^{-3}; D, 15×10^{-3} M. (*b*) Dependence of the initial rate of naphthalene oxidation (W_{Nph}^{obs}) on $[cSt]_{add}$ and its linearization.

Satisfactory linearization of the dependency of oxidation rates on the complementary substrate concentrations in reciprocal coordinates (Figs. 7(*b*), 8(*b*)), together with different k_{ol} and k_{Nph} values, evidenced that *cis*-stilbene and naphthalene were oxidized by distinct high-valent oxomanganese species

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§ With the less stable Mn-porphyrins **1**–**4** kinetic expressions of Nph disappearance at low catalyst concentrations were complicated by catalyst decomposition. Initial rates of Nph disappearace (W_{NphOH}^{in}) were determined instead.

which are formed from the same intermediate '**A**' and are in equilibrium. If the intervention of RTDCPPMn^{V}(O)(X) is admitted in the epoxidation of alkenes, kinetic data give relevant suggestions on the nature of the high-valent species involved in naphthalene hydroxylation. Three oxomanganese species, PorMn^{V}(O), PorMn^{IV}(O), and [PorMn^{IV}(O)]$^{+\bullet}$, are generally postulated as oxidizing intermediates in PorMn^{III} catalysed reactions.[16–18] The size of the experimental k_{Nph} values, close to k_{ol}, lead us to exclude the intervention of PorMn^{IV}(O) which is of very low reactivity (five orders of magnitude less reactive than [PorMn^{IV}(O)]$^{+\bullet}$).[18] On the other hand, while the very reactive PorMn^{V}(O) is also highly stereospecific in alkene epoxidation, its electronic isomer [PorMn^{IV}(O)]$^{+\bullet}$ gives mixtures of epoxides suggesting the formation of radical intermediates in the course of the epoxidation. All these data support the intervention of [PorMn^{IV}(O)]$^{+\bullet}$ in the hydroxylation of aromatic hydrocarbons.

The conclusions drawn from experimental results described above are summarized in Scheme 4, where two alternative

$$\text{(a) RTDCPPMnX} + \text{AcOOH} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathbf{A}$$

$$\text{(b) } \mathbf{A} \xrightarrow{k_2} \text{RTDCPPMn}^{V}\text{(O)(X)} + \text{AcOH} \qquad \textbf{(path 1)}$$

$$\left.\begin{array}{l}\text{(c) } \mathbf{A} \overset{K_d}{\rightleftharpoons} \mathbf{A}^{-} + \text{H}^{+} \\ \text{(d) } \mathbf{A}^{-} \xrightarrow{k'_2} \text{RTDCPPMn}^{V}\text{(O)(X)} + \text{AcO}^{-}\end{array}\right\} \textbf{(path 2)}$$

$$\text{(e) RTDCPPMn}^{V}\text{(O)(X)} \overset{K_2}{\rightleftharpoons} [\text{RTDCPPMn}^{IV}\text{(O)}]^{+\bullet}\text{(X)}$$

$$\text{(f) RTDCPPMn}^{V}\text{(O)(X)} + \text{cSt} \xrightarrow{k_3} \text{RTDCPPMnX} + \text{cStO}$$

$$\text{(g) } [\text{RTDCPPMn}^{IV}\text{(O)}]^{+\bullet}\text{(X)} + \text{Nph} \xrightarrow{k_4} \text{RTDCPPMnX} + \text{NphOH}$$

Scheme 4

pathways leading to the generation of the high-valent oxomanganese species are shown. The available data do not suffice to decide whether this happens through dissociation of the molecular complex [RTDCPPMnAcOOH](X) (adduct '**A**', path 1) or from the corresponding manganese peroxoacetate RTDCPPMnOOAc ('**A**$^{-}$', path 2). However, considering the simplest pathway of Scheme 4 (path 1) as the only possible mode of RTDCPPMn^{V}(O)(X) generation and $K_1[\text{AcOOH}]_0 > 1$, kinetic laws for the disappearance rate of *cis*-stilbene and naphthalene in competitive oxidations ($W_{ol}{}^{Nph}$ and $W_{Nph}{}^{ol}$, eqns. (3) and (4) respectively) can be obtained. They are

$$W_{ol}{}^{Nph} = \frac{k_2k_3[\text{RTDCPPMnX}]_0[\text{cSt}]_0}{(1 + K_2)(k_3[\text{cSt}]_0 + k_4[\text{Nph}]_0)} \qquad (3)$$

$$W_{Nph}{}^{ol} = \frac{k_2k_4K_2[\text{RTDCPPMnX}]_0[\text{cSt}]_0}{(1 + K_2)(k_3[\text{cSt}]_0 + k_4[\text{Nph}]_0)} \qquad (4)$$

consistent with the experimentally found correlations reported in Fig. 7(*b*) and Fig. 8(*b*).

In the absence of competing substrate, eqns. (3) and (4) become equivalent to the experimentally observed eqns. (1a) and (2a) respectively, with

$$k_{ol} = \frac{k_2}{1 + K_2} \qquad (5)$$

and

$$k_{Nph} = \frac{k_2K_2}{1 + K_2} \qquad (6)$$

According to this picture, the equilibrium constant K_2 and the elementary rate constant k_2 for the formation of the high-valent oxomanganese species could be evaluated for each catalyst from the experimentally found k_{ol} and k_{Nph} values (Table 1). However, if path 2 in Scheme 4 was involved, unknown K_d values should enter in the kinetic laws thus complicating the evaluation of k'_2. Additional studies on the nature of the first intermediate were therefore carried out, as described in the following paper.

Conclusion

Kinetic investigations of *cis*-stilbene epoxidation and of naphthalene hydroxylation with peracetic acid catalysed by five different Mn^{III} *meso*-tetra(2,6-dichloro-4-R-phenyl)porphyrins showed that both reactions proceed in two distinct steps. Reversible interactions of the catalyst with peracetic acid lead to a first intermediate '**A**' that could be a simple catalyst–oxidant adduct or a peroxoacetate complex. Transformation of '**A**' (or of the corresponding peroxocetate '**A**$^{-}$') into an equilibrium mixture of two high-valent oxomanganese species, RTDCPPMn^{V}(O)(X) and, supposedly, [RTDCPPMn^{IV}(O)]$^{+\bullet}$(X), is irreversible. The two species display unlike oxidizing activities, the former being involved in the epoxidation of *cis*-stilbene and the latter in the hydroxylation of naphthalene. The values of the rate constant k_2 for the irreversible stage could be determined from experimentally found k_{ol} and k_{Nph} values, assuming that intermediate '**A**' was a catalyst–oxidant molecular adduct. Further studies on the nature of this species and on the mechanism of RTDCPPMnX interactions with peracetic acid will be presented in the following paper.

Experimental

GC analyses were performed on a "Tsvet-100" instrument (Columns: Apiezon L 2 m, $T_{col} = T_{inj} = 200$ °C, or OV 225 2 m, $T_{col} = 130$ °C, $T_{inj} = 150$ °C; carrier gas = He) equipped with a computing integrator C1-100. High performance liquid chromatography analyses were performed on a "Millichrom-1A" instrument (Silosorb C_{18} reversed-phase column) supplied with a computing integrator C1-100 and UV detector (λ_{anal} 230 and 280 nm for 1- and 2-naphthols and naphthalene, respectively). Mobile phase: (a) gradient 0 to 100% CH_3CN in aqueous 0.01 M KH_2PO_4 adjusted to pH 3 with H_3PO_4 or (b) 10–100% aqueous CH_3CN. Reaction products were identified by coinjection of the reaction solution with authentic samples onto HPLC or GC columns. The positive ion FAB mass spectra were obtained with a Finnigan-MAT90 mass spectrometer, standard FAB source and an Ion Tech atom gun (Xe, 5×10^{-5} mPa, 8 keV, 20 μA) at better than unit resolution; commercially available 3-nitrobenzyl alcohol or thioglycerol was used as matrix. Naphthalene and *cis*-stilbene (Aldrich) were used as received. Acetonitrile (HPLC grade) was additionally purified by distillation on potassium permanganate, then kept for 24 h over $CaCl_2$ and 24 h on BaO. Solutions of peracetic acid in acetic acid (1.3–1.9 M) were prepared as previously reported.[14] Mn-porphyrins were dissolved in CH_3CN by gentle heating (30–40 min, 40–50 °C). In all experiments, reagent solutions were prepared prior to use. Elemental analyses were performed by Departmental Service of Microanalysis (University of Milano).

Synthesis of RTDCPPMnCl (compounds 1–5)

All porphyrins were prepared by condensation of the corresponding substituted benzaldehyde (10 mmol) with pyrrole (10 mmol) according to published procedures.[31] The corresponding Mn complexes were obtained by refluxing a solution of the porphyrin (0.15 mmol) in DMF (25 cm^3) with an excess of $Mn(OAc)_2 \cdot 4H_2O$ (0.9 mmol).[32] Preparation details for new compounds are given below, together with physical data.

[5,10,15,20-Tetrakis(2,6-dichloro-4-methoxyphenyl)-porphyrinato]manganese(III) chloride 1. Condensation of 2,6-dichloro-5-methoxybenzaldehyde[33] (2.05 g, 10 mmol) with pyrrole (0.67 g, 10 mmol) (solvent = CH_2Cl_2, catalyst = BF_3·Et_2O, oxidant = *p*-chloranil) followed by chromatography on silica gel with CH_2Cl_2–light petroleum (bp 40–60 °C) (7 : 3) as the eluent and precipitation from CH_2Cl_2–pentane afforded the free-base porphyrin (0.763 g, 30%) (Found: C, 57.2; H, 2.85; N, 5.5. $C_{48}H_{30}Cl_8N_4O_4$ requires C, 57.05; H, 3.0; N, 5.55%); λ_{max} (CH_2Cl_2)/nm 418 (ε/dm^3 mol^{-1} cm^{-1} 2.70 × 10^5); δ_H(300 MHz; $CDCl_3$) −2.60 (br s, 2 H), 4.08 (s, 12 H), 7.33 (s, 8 H), 8.69 (s, 8 H); *m*/*z* 1010 (M$^+$, 100%).

A solution of porphyrin (150 mg, 0.15 mmol) in DMF (25 cm^3) was stirred for 7 h under reflux with $Mn(OAc)_2$·$4H_2O$ (220 mg, 0.9 mmol). After evaporation of DMF under reduced pressure the residue was taken up in CH_2Cl_2 (50 cm^3), washed with water (2 × 15 cm^3) and saturated aqueous NaCl (2 × 15 cm^3) and dried over $MgSO_4$. Chromatography on silica gel with $CHCl_3$–MeOH (95 : 5) as the eluent, followed by precipitation from CH_2Cl_2–pentane, afforded **1** as a dark brown powder (123 mg, 75%) (Found: C, 52.35; H, 2.75; N, 5.0. $[C_{48}H_{28}Cl_8N_4O_4Mn]^+Cl^-$ requires C, 52.5; H, 2.6; N, 5.1%); λ_{max} (CH_2Cl_2)/nm 478 (ε/dm^3 mol^{-1} cm^{-1} 1.36 × 10^5); *m*/*z* 1063 (M$^+$, 100%) for $[C_{48}H_{28}Cl_8N_4O_4Mn]^+$.

4-Bromo-2,6-dichlorotoluene. 3,5-Dichloro-4-methylaniline[34] (3.17 g, 18 mmol) was added to a solution of 48% HBr (5.4 cm^3) in H_2O (5 cm^3). The suspension was gently heated till a clear solution was obtained then cooled to 0 °C. A solution of $NaNO_2$ (1.30 g, 19 mmol) in H_2O (3 cm^3) was added dropwise under stirring, keeping the temperature below 5 °C. After 10 min the diazonium salt solution was poured into a mixture of freshly distilled 48% HBr (20 cm^3) and CuBr (12.9 g, 90 mmol). After 0.5 h at 50 °C, the mixture was cooled to room temperature and extracted with CH_2Cl_2 (4 × 15 cm^3). The organic layer was filtered on Celite, dried on Na_2SO_4 and evaporated to dryness. Flash chromatography on silica gel with light petroleum as the eluent yielded 4-bromo-2,6-dichlorotoluene (2.25 g, 52%), mp 45–46 °C (Found: C, 40.95; H, 2.2. $C_7H_5BrCl_2$ requires C, 41.1; H, 2.45%); δ_H(80 MHz; $CDCl_3$) 2.39 (s, 3 H), 7.42 (s, 2 H).

4-Bromo-2,6-dichlorobenzyl bromide. To a solution of 4-bromo-2,6-dichlorotoluene (1.2 g, 5 mmol) in CCl_4 (15 cm^3) *N*-bromosuccinimide (1 g, 5.6 mmol) was added. The suspension was brought to reflux under irradiation with a common 300 W lightbulb for 2 h. After cooling, succinimide was filtered off and the filtrate evaporated to dryness. Chromatography on silica gel with light petroleum as the eluent yielded 4-bromo-2,6-dichlorobenzyl bromide (1.53 g, 96%), mp 58 °C (Found: C, 26.6; H, 1.2. $C_7H_4Br_2Cl_2$ requires C, 26.4; H, 1.25%); δ_H(80 MHz; $CDCl_3$) 4.65 (s, 2 H), 7.50 (s, 2 H).

4-Bromo-2,6-dichlorobenzyl alcohol. To a solution of 4-bromo-2,6-dichlorobenzyl bromide (3.19 g, 10 mmol) in CH_3CN (50 cm^3) solid CH_3COOK (4.8 g, 40 mmol) was added. The solution was stirred at room temperature for 12 h. The solid was filtered off and the filtrate evaporated to dryness. The crude 4-bromo-2,6-dichlorobenzyl acetate thus formed was suspended in boiling EtOH (50 cm^3) and hydrolysed with NaOH (1g, 25 mmol) in H_2O (7 cm^3). After 1 h the suspension was cooled to room temperature and extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4 and evaporated to dryness yielding 4-bromo-2,6-dichlorobenzyl alcohol (2.35 g, 92%), mp 104–106 °C (Found: C, 32.65; H, 1.7. $C_7H_5BrCl_2O$ requires C, 32.85; H, 2.0%); δ_H(80 MHz; $CDCl_3$) 2.1 (bs, 1 H), 4.80 (bs, 2 H), 7.48 (s, 2 H).

4-Bromo-2,6-dichlorobenzaldehyde. A solution of 4-bromo-2,6-dichlorobenzyl alcohol (1.28 g, 5 mmol) in $CHCl_3$ (60 cm^3) was oxidized with MnO_2 (3.75 g, 41 mmol) at reflux for 18 h. The solid was filtered off and the liquid phase evaporated to dryness. Chromatography on silica gel with light petroleum–Et_2O (3 : 2) as the eluent yielded 4-bromo-2,6-dichlorobenzaldehyde **13** (0.7 g, 55%), mp 56–57 °C (Found: C, 33.0; H, 1.1. $C_7H_3BrCl_2O$ requires C, 33.1; H, 1.2%); δ_H(80 MHz; $CDCl_3$) 7.55 (s, 2 H), 10.35 (s, 1 H).

[5,10,15,20-Tetrakis(4-bromo-2,6-dichlorophenyl)porphyrinato]manganese(III) chloride 3. Condensation of 4-bromo-2,6-dichlorobenzaldehyde with pyrrole was carried out as described for porphyrin **1**. Flash chromatography on silica gel with CH_2Cl_2–light petroleum (1 : 1) as the eluent afforded the free-base porphyrin which was then washed with cold CCl_4 (20%) (Found: C, 43.6; H, 1.65; N, 4.85. $C_{44}H_{18}Br_4Cl_8N_4$ requires C, 43.8; H, 1.5; N, 4.65%); λ_{max} (CH_2Cl_2)/nm 418 (ε/dm^3 mol^{-1} cm^{-1} 2.93 × 10^5); δ_H(300 MHz; $CDCl_3$) −2.65 (s, 2 H), 7.97 (s, 8 H), 8.67 (s, 8 H); *m*/*z* 1205 (M$^+$, 100%).

Insertion of manganese was carried out as described for porphyrin **1**. Chromatography on silica gel with $CHCl_3$–MeOH (9 : 1) as the eluent, followed by precipitation from CH_2Cl_2–pentane, afforded complex **3** as a dark brown powder (80%) (Found: C, 40.65; H, 1.4; N, 4.2. $[C_{44}H_{16}Br_4Cl_8N_4Mn]^+Cl^-$ requires C, 40.8; H, 1.25; N, 4.3%); λ_{max} (CH_2Cl_2)/nm 474 (ε/dm^3 mol^{-1} cm^{-1} 1.33 × 10^5); *m*/*z* 1258 (M$^+$, 100%) for $[C_{44}H_{16}Br_4Cl_8N_4Mn]^+$.

[5,10,15,20-Tetrakis(2,4,6-trichlorophenyl)porphyrinato]manganese(III) chloride 4. Under the conditions reported for porphyrin **1**, 2,4,6-trichlorobenzaldehyde,[35] obtained from 2,4,6-trichlorotoluene[36] as described for 4-bromo-2,6-dichlorobenzaldehyde, was condensed with pyrrole. Flash chromatography on silica gel with CH_2Cl_2–light petroleum (1 : 1) as the eluent and precipitation from CH_2Cl_2–pentane afforded the free-base porphyrin (25%) (Found: C, 51.3; H, 1.7; N, 5.3. $C_{44}H_{18}Cl_{12}N_4$ requires C, 51.4; H, 1.75; N, 5.45%); λ_{max} (CH_2Cl_2)/nm 419 (ε/dm^3 mol^{-1} cm^{-1} 2.70 × 10^5); δ_H(300 MHz; $CDCl_3$) −2.65 (s, 2 H), 8.10 (s, 8 H), 8.71 (s, 8 H); *m*/*z* 1028 (M$^+$, 100%).

Insertion of manganese was carried out as described for porphyrin **1**. Chromatography on silica gel with $CHCl_3$–MeOH (9 : 1) as the eluent, followed by precipitation from CH_2Cl_2–pentane afforded complex **3** as a dark brown powder (78%) (Found: C, 47.45; H, 1.3; N, 4.85. $[C_{44}H_{16}Cl_{12}N_4Mn]^+Cl^-$ requires C, 47.35; H, 1.45; N, 5.0%); λ_{max} (CH_2Cl_2)/nm 479 (ε/dm^3 mol^{-1} cm^{-1} 1.28 × 10^5); *m*/*z* 1081 (M$^+$, 100%) for $[C_{44}H_{16}N_4Cl_{12}Mn]^+$.

[5,10,15,20-Tetrakis(2,6-dichloro-4-nitrophenyl)porphyrinato]manganese(III) chloride 5. The manganese complex was synthesized from the corresponding free-base porphyrin[37] according to the procedure described for **1**. Column chromatography on silica gel with CH_2Cl_2–MeOH (8 : 1) yielded pure **5** (83%) (Found: C, 45.45; H, 1.5; N, 9.5. $[C_{44}H_{16}Cl_8N_8O_8Mn]^+Cl^-$ requires C, 45.6; H, 1.4; N, 9.7%); λ_{max} (CH_2Cl_2)/nm 480 (ε/dm^3 mol^{-1} cm^{-1} 1.21 × 10^5); *m*/*z* 1119 (M$^+$, lowest-mass peak of isotope cluster) for $[C_{44}H_{16}Cl_8N_8O_8Mn]^+$.

Epoxidation of *cis*-stilbene

In all experiments the mother solutions of *cis*-stilbene, RTD-CPPMnCl and AcOOH were prepared at concentrations three times those desired in the reaction mixture. A typical procedure is described. In a Schlenk tube were added in order: 1 ml of a CH_3CN solution (0.03 M) of the alkene, 1 ml of a CH_3CN solution (3 × 10^{-5} M) of catalyst **4** and 1 ml of a solution of AcOOH (0.00375 M) in AcOH–CH_3CN (1.31 M AcOOH in AcOH diluted 35 times with CH_3CN). In the case of reactions carried out at $[AcOH]_0$ = const. (see Fig. 2), AcOOH solution in CH_3CN was prepared with the desired amount of AcOH. The solution was stirred at 20 °C. Samples of 0.2 ml were withdrawn at fixed times, the excess of AcOOH was quenched with solid tetrabutylammonium iodide and the mixture analysed by GC (OV 225 × 2 m column). The amount of substrate and products was determined using calibration curves obtained with authentic samples.

Hydroxylation of naphthalene

Reactions were carried out at 20 °C as described for *cis*-stilbene epoxidation. Naphthalene disappearance was measured by GC (OV 225 × 2 m column) after quenching the excess of AcOOH with tetrabutylammonium iodide. The formation of 1- and 2-naphthols was measured by HPLC without quenching the excess of AcOOH: 5–10 μl aliquots of the reaction mixture were injected directly. The amount of substrate and products was determined using calibration curves obtained with authentic samples.

Competitive oxidation of naphthalene and *cis*-stilbene

In all experiments the mother solutions of *cis*-stilbene, naphthalene, RTDCPPMnCl and AcOOH in CH_3CN were prepared at concentrations four times those desired in the reaction mixture. Reactions were then carried out as in the case of a single substrate. The amounts of *cis*-stilbene, *cis*-stilbene epoxide and naphthalene were measured by GC after quenching with tetrabutylammonium iodide, while NphOH formation was monitored by HPLC.

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