

Kinetic studies on the interactions of manganese–porphyrins with peracetic acid. Part 2.¹ The influence of acetic acid and porphyrin substituents

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Received (in Cambridge, UK) 3rd September 1999, Accepted 11th February 2000

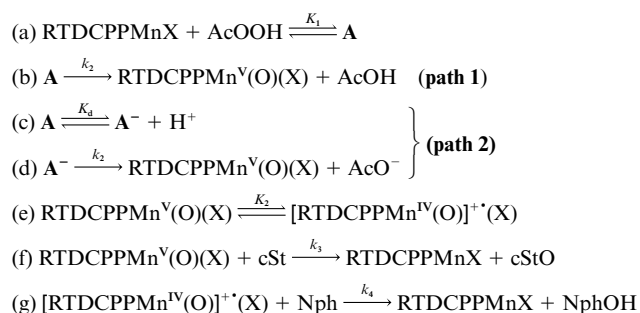
The one-electron oxidation of 1,1-diphenyl-2-picrylhydrazine (DPPH) and Zn–tetra-*tert*-butylphthalocyanine (PcZn) to the corresponding stable radical (DPP[•]) and π -radical cation (PcZn^{•+}) with peracetic acid in acetonitrile–acetic acid has been studied, in the presence of Mn^{III} complexes of *meso*-tetra(2,6-dichloro-4-*R*-phenyl)porphyrins (RTDCPPMnCl; R = CH₃O, H, Br, Cl or NO₂) as catalysts. The formation of a two-centre donor–acceptor complex of "catalyst–oxidant" type (adduct 'A') with rate constant k_1 is the first stage of the reaction. The balance of the electron donating properties of the porphyrin ring and electron accepting properties of Mn^{III} determines the formation of 'A', as shown by the independence of k_1 of catalyst structure. The influence of added acetic acid on the UV–Vis spectra of RTDCPPMnX in CH₃CN and on the oxidation rate of DPPH and PcZn evidenced that a molecule of AcOH is included in the internal co-ordination sphere of RTDCPPMnX and of the reaction intermediates. The rate constant k_2 for the irreversible transformation of 'A' into an equilibrium mixture of Mn^V and Mn^{IV} oxo-species (established in Part 1) must thus refer to the acetic acid adducts of Mn–porphyrins {[RTDCPPMn(AcOH)](X)}. A non-linear dependence of log k_2^{rel} on σ_{para} of the porphyrin substituents R has also been found. However, electron-withdrawing substituents are particularly effective for enhancement of the rate of formation of the high-valent oxomanganese species.

Introduction

The mechanism of peracetic acid interaction with Mn^{III} complexes of *meso*-tetra(2,6-dichloro-4-*R*-phenyl)porphyrins (RTDCPPMnCl; R = CH₃O **1**, H **2**, Br **3**, Cl **4** or NO₂ **5**. See Part 1, Fig. 1) in acetonitrile–acetic acid solutions involves the reversible formation of an intermediate complex of "catalyst–oxidant" type.¹ Using *cis*-stilbene (cSt) and naphthalene (Nph) as the substrates both in separate and competitive catalytic oxidations, it was demonstrated that further irreversible transformation of this intermediate with elementary rate constant k_2 leads to an equilibrium mixture of RTDCPPMn^V(O)(X) and, supposedly, [RTDCPPMn^{IV}(O)]⁺(X). The former is responsible for *cis*-stilbene epoxidation and the latter for the hydroxylation of naphthalene (Scheme 1). However, these investigations

did not elucidate the nature of the first intermediate which could be either a molecular complex ([RTDCPPMn–AcOOH]–(X), 'A', path 1, Scheme 1) or the corresponding manganese–peroxoacetate (RTDCPPMnOOAc, 'A[–]', path 2, Scheme 1). Solving this problem is important for the correct calculation of k_2 values, which would give hints for the rational design of Mn^{III}–porphyrins featuring optimum catalytic properties in oxidation reactions.

As discussed in the preceding paper, the experimental rate constant values for *cis*-stilbene and naphthalene oxidation (k_{ol} and k_{Nph}) could easily be correlated with k_2 by using the kinetic expressions for the rate of *cis*-stilbene and naphthalene disappearance in competitive oxidations ($W_{\text{ol}}^{\text{Nph}}$ and $W_{\text{Nph}}^{\text{ol}}$ respectively), obtained assuming the validity of path 1 and $K_1[\text{AcOOH}]_0 > 1$.¹ However, the intervention of path 2 in the reaction mechanism could not be rejected on the basis of the available experimental data. In this case, the kinetic expressions for $W_{\text{ol}}^{\text{Nph}}$ and $W_{\text{Nph}}^{\text{ol}}$ would take into account the equilibrium constant K_d for the dissociation of 'A'. In the absence of competing substrate and assuming $K_1[\text{AcOOH}]_0 > 1$ and $K_d < 1$, eqns. (1) and (2) can be derived, from which direct estimation of k'_2 , K_d , K_2 from k_{ol} and k_{Nph} is obviously precluded.



Scheme 1

$$k_{\text{ol}} = \frac{k'_2 K_d}{1 + K_2} \quad (1)$$

$$k_{\text{Nph}} = \frac{k'_2 K_2 K_d}{1 + K_2} \quad (2)$$

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We here describe further investigations aimed at establishing whether the first intermediate 'A' can dissociate. To this pur-

Table 1 Reagent concentrations and experimental rate constant values k_1 for 1,1-diphenyl-2-picrylhydrazine (DPPH) and Zn tetra-*tert*-butylphthalocyanine (PcZn) oxidation with peracetic acid catalysed by RTDCPPMnCl **1–5** at 20 °C^{a,b}

Catalyst	$10^6[\text{Catalyst}]_0/\text{mol dm}^{-3}$	$[\text{DPPH}]_0/\text{mol dm}^{-3}$	$10^5[\text{PcZn}]_0/\text{mol dm}^{-3}$	$10^5[\text{AcOOH}]_0/\text{mol dm}^{-3}$	$[\text{AcOH}]_0/\text{mol dm}^{-3}$	$k_1/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
1	0.20–10	$(1-200) \times 10^{-5}$	0.14–0.83	2–5 ^c	0.01–0.05 ^c	200 ^c
				1.9–9.5 ^d	0.1–0.2 ^d	220 ^d
2	0.14–10	$(1-2) \times 10^{-3}$	0.3–0.85	2–5 ^c	0.006–0.1 ^c	210 ^c
				1.2–9.5 ^d	0.005–0.3 ^d	200 ^d
3	2–5	2×10^{-3}	0.88–1.54	5 ^c	0.025–0.05 ^c	260 ^c
				2–4.7 ^d	0.05–0.2 ^d	250 ^d
4	0.05–10	2×10^{-3}	0.23–1.13	2–5 ^c	0.005–0.1 ^c	220 ^c
				4.8–9.6 ^d	0.1–0.4 ^d	210 ^d
5	0.12–1.0	$(1-200) \times 10^{-5}$	0.15–0.9	5 ^c	0.025–0.08 ^c	230 ^c
				0.12–0.95 ^d	0.01–0.4 ^d	200 ^d

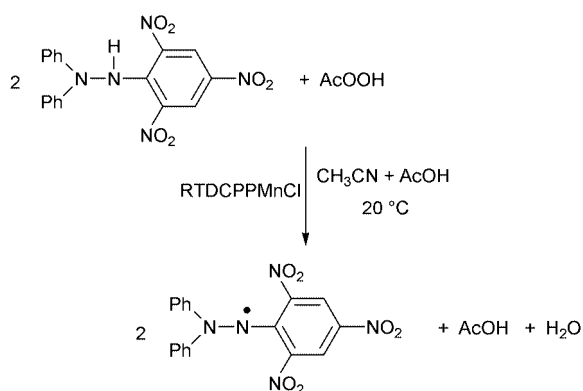
^a Reaction conditions: see ref. 1. $[\text{AcOH}]_0 : [\text{RTDCPPMnCl}]_0 \geq 1000 : 1$. Several measurements were done within the concentration ranges shown. To avoid competitive radical peracid decomposition $[\text{AcOOH}]_0 \leq 10^{-4}$ M was used. ^b For DPPH oxidation the contribution of the non-catalysed reaction (see text) was subtracted from the overall reaction rates. Reaction rates for PcZn oxidation were uncorrected (contribution of the non-catalysed reaction about 2%). Experimental error in k_1 determination is $\pm 10\%$ rel. ^c DPPH oxidation, $k_1 = k_g$ (eqn. 5). ^d PcZn oxidation, $k_1 = k_{\text{Pc}}$ (eqn. 7).

pose the influence of acetic acid concentration on the kinetics of the one-electron oxidation of 1,1-diphenyl-2-picrylhydrazine (DPPH) and zinc-tetra-*tert*-butylphthalocyanine (PcZn)² was studied, as well as the influence of other acids on the kinetics of *cis*-stilbene and naphthalene oxidation.

Results and discussion

1,1-Diphenyl-2-picrylhydrazine one-electron oxidation

It was previously shown that DPPH acts as a scavenger for intermediate 'A' in PorMnX (PorMnX = **2** or Mn-azaporphines) catalysed oxidations and also as a scavenger for the molecular complexes of phthalocyanines with benzoyl peroxide.^{3,4} Indeed, in the presence of an excess of DPPH, the rate of the corresponding stable radical (DPP[•]) formation (W_{DPP}) is proportional to the rate of the primary interaction of the catalyst with the oxidant. As a consequence, if [RTDCPPMn–AcOOH]–(X) and RTDCPPMnOOAc displayed different activities in DPPH oxidation, W_{DPP} would be influenced by $[\text{H}^+]$ in solution, since the equilibrium between the two species should be shifted to the left by addition of acids (Scheme 1). It should also be pointed out that DPPH undergoes one-electron oxidation (Scheme 2) in the absence of any catalyst. However, the reaction



rate is sensibly increased by the addition of metallo-porphyrins and the contribution of catalytic and non-catalytic processes can be recognized.³

The influence of $[\text{AcOH}]_0$ on DPPH oxidation by AcOOH in the absence of any catalyst was first determined at $[\text{DPPH}]_0 \geq 0.001$ M and $[\text{AcOOH}]_0 \leq 0.001$ M. Peracetic acid (AcOOH) solutions in CH_3CN used in this work were prepared from known aliquots of 1.3–1.7 M mother solutions of

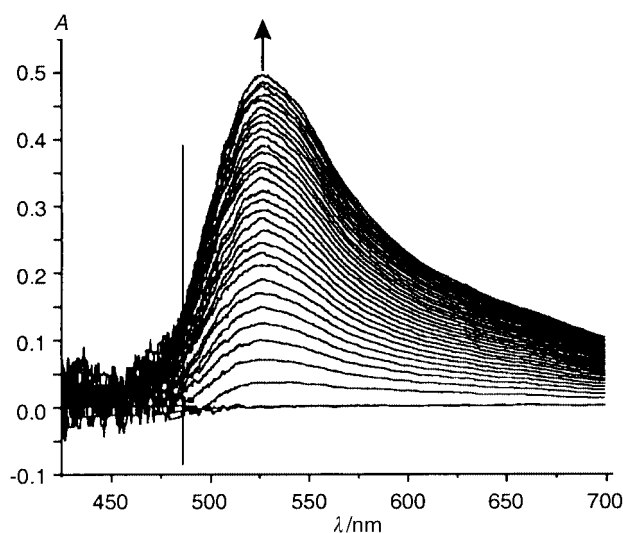


Fig. 1 Difference UV–Vis spectra (absorbance of the solution at time τ – absorbance of the solution at $t=0$) of the reaction solution in DPPH oxidation with AcOOH catalysed by **3**. $[\text{DPPH}]_0 = 2 \times 10^{-3}$ M, $[\mathbf{3}]_0 = 5 \times 10^{-6}$ M, $[\text{AcOOH}]_0 = 4 \times 10^{-5}$ M, $[\text{AcOH}]_0 = 0.025$ M. Time intervals 15 s. $\epsilon_{\text{DPP}}^{535 \text{ nm}} = 1.5 \times 10^4 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, $l = 1$ cm.

AcOOH in AcOH.¹ The concentration of AcOH added with the oxidant ($[\text{AcOH}]_{\text{ox}}$) was consequently about ten times $[\text{AcOOH}]_0$. In order to vary $[\text{AcOH}]_0$, known volumes of AcOH were added to the CH_3CN solutions of the reagents: $[\text{AcOH}]_0$ is thus defined as $[\text{AcOH}]_{\text{ox}} + [\text{AcOH}]_{\text{add}}$.

It was found that the rate of non-catalysed reaction (W_{nc}) is independent of $[\text{AcOH}]_0$ up to 0.1 M; at $[\text{AcOH}]_0 \geq 0.1$ M the rate of DPP[•] formation decreases due to DPPH protonation and becomes proportional to $[\text{AcOH}]_0^{-0.5}$. Hence, $[\text{AcOH}]_0$ in DPPH oxidation can not exceed 0.1 M with $[\text{DPPH}]_0 \geq 0.001$ M to provide $[\text{DPPH}]_{\text{free}} \gg [\text{DPPH}]_{\text{protonated}}$.

At $[\text{AcOH}]_0 = 0.01$ –0.1 M, with other reagent concentrations shown in Table 1 and in the presence of catalysts **1–5** DPPH was oxidized to DPP[•] with yields η up to 90–100% with respect to $[\text{AcOOH}]_0$ ($\eta = \{2[\text{DPP}^{\bullet}]/[\text{AcOOH}]_0\} \times 100$). The characteristic UV–Vis absorption of the catalyst did not change all along the reaction, whereas the absorption of DPP[•] regularly increased up to the maximum value. Difference UV–Vis spectra (absorbance of the solution at time τ – absorbance of the solution at $t=0$) for the catalytic oxidation of DPPH in the presence of catalyst **3** are reported in Fig. 1.

The rate of DPP[•] formation was found to be first order both in $[\text{AcOOH}]_0$ and $[\text{RTDCPPMnX}]_0$ and independent of the substrate concentration at $[\text{DPPH}]_0 \geq 10^{-3}$ M. This result

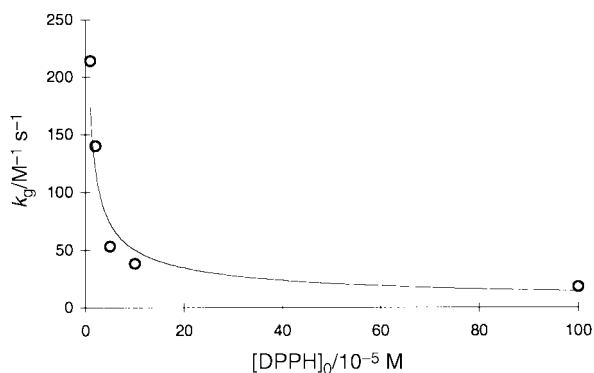
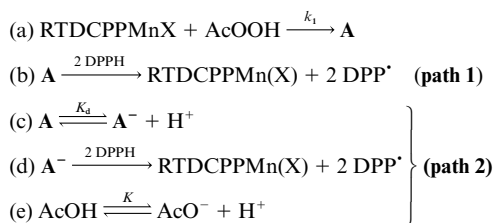


Fig. 2 Dependence of DPP' formation rate constant ($k_g = W_{\text{DPP}}/2\{[1]_0[\text{AcOOH}]_0\}$) on $[\text{DPPH}]_0$ in the reaction catalysed by **1**. $[1]_0 = (0.1-1) \times 10^{-5}$ M, $[\text{AcOOH}]_0 = (0.25-1) \times 10^{-5}$ M, $[\text{AcOH}]_{\text{ox}} = (0.3-1) \times 10^{-4}$ M.

confirms that DPPH acts as a real trap for the oxidative intermediate, *i.e.* the first reaction stage becomes irreversible and the rates of DPP' and 'A' (or 'A⁻') formation are equal taking into account the stoichiometric coefficient 2 (Scheme 2).³ The experimentally determined bimolecular rate constant of DPP' formation k_g can be thus correlated to the elementary rate constant k_1 by eqn. (3) or (4) derived from Scheme 3, which are

$$k_g = \frac{W_{\text{DPP}}}{2 [\text{RTDCPPMnX}]_0 [\text{AcOOH}]_0} = k_1 \quad (3)$$

$$k_g = \frac{W_{\text{DPP}}}{2 [\text{RTDCPPMnX}]_0 [\text{AcOOH}]_0} = \frac{k_1 K_d}{(K [\text{AcOH}]_0)^{0.5} + K_d} \quad (4)$$



Scheme 3

valid when path 1 or 2 is followed respectively. As shown in Table 1, k_g values calculated according to eqn. (3) do not depend on $[\text{AcOH}]_0$ at $0.01 \leq [\text{AcOH}]_0 \leq 0.1$ M, as expected if path 1 (Scheme 3) were followed. However, this concentration range is too narrow to exclude the involvement of path 2 in the mechanism. Further attempts to study the influence of $[\text{AcOH}]_0$ at lower concentrations were frustrated by a rather unexpected finding.

At $[\text{AcOH}]_0 \leq 0.005$ M the mechanism of DPPH oxidation dramatically changes. The rate of DPP' formation decreases with the increase of $[\text{DPPH}]_0$ (Fig. 2) and the DPP' maximum yield drops to 60% at $[\text{DPPH}]_0 \geq 10^{-4}$ M. A plausible reason for this behaviour resides in the change of the co-ordination sphere of Mn-porphyrins (and intermediate 'A') on lowering $[\text{AcOH}]_0$. Indeed, AcOH could play the role of axial ligand in the active form of 'A' generated from $[\text{RTDCPPMn}(\text{AcOH})](\text{X})$, in analogy to imidazole and other N-heterocyclic bases in the well-known PorMnX + NaOCl catalytic system⁵ and modifications.⁶ A similar effect of carboxylic acid was proposed in catalytic oxidations with $\text{PorMnX} + \text{H}_2\text{O}_2 + \text{C}_6\text{H}_5\text{COOH}$.⁷ The axial co-ordination of Mn-porphine complexes with O containing molecules is well-known.^{8a,9,10} It is also known that changing the nature of the axial ligand leads to variations in the electron density distribution between the macrocycle and the complexed metal ion in high-valent (+4 and +5) oxometallo species.¹¹ The strong influence of the nature of the axial ligand

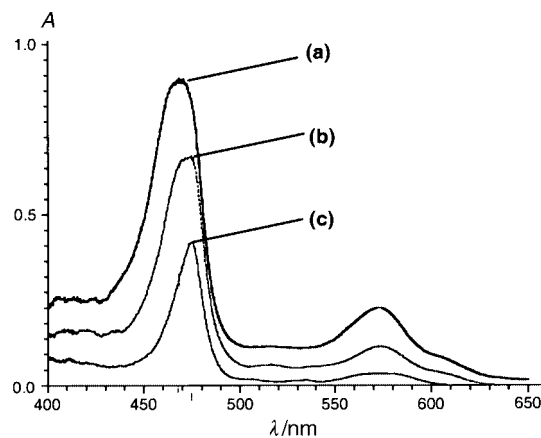


Fig. 3 UV-Vis spectral changes for a CH_3CN solution of RTDCPP-MnOAc (**2a**) upon dilution. (a) $[\mathbf{2a}] = 0.9 \times 10^{-4}$ M, $l = 0.2$ cm; (b) $[\mathbf{2a}] = 0.9 \times 10^{-5}$ M, $l = 1$ cm; (c) $[\mathbf{2a}] = 0.45 \times 10^{-5}$ M, $l = 1$ cm.

(imidazole, thiolate or chloride anions, methanol, mineral and carboxylic acids) on the electronic structure of the oxoiron complex produced by iron porphyrins interaction with peracids has recently been documented.⁸ At low $[\text{AcOH}]_0$, the interaction of RTDCPPMnX with CH_3CN or DPPH in excess could lead subsequently to a less active form of intermediate 'A', in which CH_3CN (or DPPH) plays the role of the axial ligand instead of AcOH. This species would not produce DPP' in its interaction with a second DPPH molecule, thus lowering both reaction rates and DPP' yields.

Influence of AcOH on the UV-Vis spectra of RTDCPPMnX

In order to find experimental evidence for the inclusion of AcOH into the internal co-ordination sphere of RTDCPP-MnX, the influence of $[\text{AcOH}]_0$ on the UV-Vis spectra of RTDCPPMnX in CH_3CN as well as the influence of acid strength on the rates of *cis*-stilbene and naphthalene oxidation were investigated. The UV-Vis spectra of Mn complexes **1-5** (10^{-4} – 10^{-6} M) in pure CH_3CN are modified by dilution (Fig. 3 for TDCPPMnOAc **2a**) and the absorbance of the Soret band does not obey Lambert-Beer's law at concentrations higher than 10^{-5} M. Such a behaviour was observed for *meso*-substituted porphyrins both in water and in organic solvents and imputed to aggregation.¹² The UV-Vis spectra of Mn-complexes **1-5** change upon addition of AcOH (from 0.005 to 0.5 M), as exemplified in Fig. 4. At $[\text{AcOH}]:[\text{RTDCPPMnX}] \geq 10^3:1$ the absorbance values of the Soret band (475 nm for **1-5**) become directly proportional to the Mn-porphyrin concentration (*i.e.* the Lambert-Beer relationship is obeyed). These spectral changes can not be explained simply by counter anion (Cl^-/AcO^-) exchange since they were observed also with TDCPPMnOAc **2a** (Fig. 4). In addition, Mn^{III}-*meso*-tetra-(2,4,6-trimethylphenyl)porphyrin (TMsPMnCl) is known to be fully dissociated in CH_3CN solution, with the insertion of a solvent molecule into the internal co-ordination sphere and the counter anion localized in the outer sphere: $[\text{TMsPMn(L)}](\text{Cl}^-)$, $\text{L} = \text{CH}_3\text{CN}$ or DMSO.¹³ We can conclude that at $[\text{AcOH}]_0:[\text{RTDCPPMnX}]_0 \geq 10^3:1$ acetic acid completely destroys porphyrin aggregates, possibly by replacement of the acetonitrile molecule in the internal co-ordination sphere of the initial complex $[\text{RTDCPPMn}(\text{CH}_3\text{CN})](\text{Cl}^-)$ to give the corresponding adduct $[\text{RTDCPPMn}(\text{AcOH})](\text{X})$ ($\text{X} = \text{Cl}^-$ or AcO^-). The interaction of this adduct with AcOOH leads to the formation of the active form of intermediate 'A' in DPPH oxidation.

Influence of acids on the rates of *cis*-stilbene and naphthalene oxidation

In some catalytic systems an increase of PorMnX activity was observed upon addition of protic acids. The acceleration of the

Table 2 Reagent concentrations and experimental rate constant values (k_{obs}) for *cis*-stilbene epoxidation with peracetic acid catalysed by RTDCPPMnCl **5** at 20 °C, in the presence of trichloroacetic acid (TCA), *p*-nitrobenzoic acid (NBA) or HClO₄^a

Entry	Acid	[AcOOH] ₀ /mol dm ⁻³	[acid] ₀ /mol dm ⁻³	k_{obs}^b /s ⁻¹
0	—	0.05	—	0.85
1	TCA	0.05	0.5×10^{-4}	0.86
2	TCA	0.05	1.25×10^{-4}	0.52
3	TCA	0.05	2.5×10^{-4}	0
4	TCA	0.05	5×10^{-4}	0
5	TCA	0.0125	1.25×10^{-4}	0.12
6	NBA	0.05	1.25×10^{-4}	2.6
7	NBA	0.05	2.5×10^{-4}	2.4
8	NBA	0.025	1.25×10^{-4}	1.0
9	HClO ₄	0.05	0.625×10^{-5}	0.92
10	HClO ₄	0.05	1.25×10^{-5}	0.56
11	HClO ₄	0.05	2.5×10^{-5}	0.23
12	HClO ₄	0.025	1.25×10^{-5}	0.6

^a Reaction conditions: see ref. 1. [AcOH]₀ = 0.5 M. ^b $k_{\text{obs}} = W_{\text{ol(ep)}/[5]_0}$.

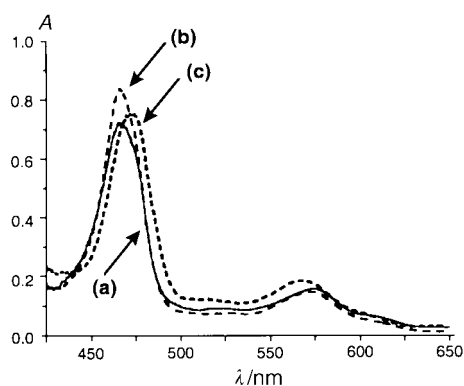


Fig. 4 Influence of acetic acid addition on the UV-Vis spectra of a CH₃CN solution of RTDCPPMnOAc. [2a] = 1.35×10^{-4} M, *l* = 0.1 cm; [AcOH]₀ = 0 (a), 0.015 (b), (c) 0.3 M.

stage of high-valent oxometal species formation is a possible explanation for this finding.^{7,14} However, the influence of acids could be exhibited at the very beginning of the oxidation reaction either by changing the PorMnX co-ordination sphere (as discussed above) or by shifting the equilibrium (c) in Scheme 1. In order to evaluate these hypotheses, the influence of different acids [H₃PO₄, HClO₄, *p*-nitrobenzoic acid (NBA) and trichloroacetic acid (TCA)] on the rate of oxidation reactions catalysed by **2** was studied. *cis*-Stilbene and naphthalene were chosen as substrates instead of DPPH, because the basicity of the latter could alter the results.

As shown in Table 2 and Fig. 5, the dependence of *cis*-stilbene and naphthalene oxidation rates on acid concentration varies according to the nature of the acid: H₃PO₄, HClO₄ and TCA inhibit oxidation rates (Fig. 5; Table 2, entries 1–4 and 9–11), while *p*-nitrobenzoic acid accelerates the reactions (Table 2, entries 6–8). Furthermore, these alterations were accompanied by changes of oxidation rates depending on [AcOOH]₀ in the case of the carboxylic acids TCA and NBA (Table 2, lines 2,5 and 6,8).

The influence of acids may be explained by the insertion of one (NBA, TCA) or two (H₃PO₄, HClO₄) molecules of acid into the internal co-ordination sphere. In the case of mineral acids (H₃PO₄, HClO₄) protonated porphyrin complexes might also be formed in the likeness of their non-metallic analogues,¹⁵ thus diminishing the [RTDCPPMn(AcOH)](X) stationary state concentration. However, UV-Vis spectra of **2** (1×10^{-5} M) were insensitive to the addition of HClO₄ or H₃PO₄ up to 30-fold molar excess. Taking also into account the weak ligand field of perchlorate anion, co-ordination of undissociated acid molecules seems to be the more reasonable hypothesis. The

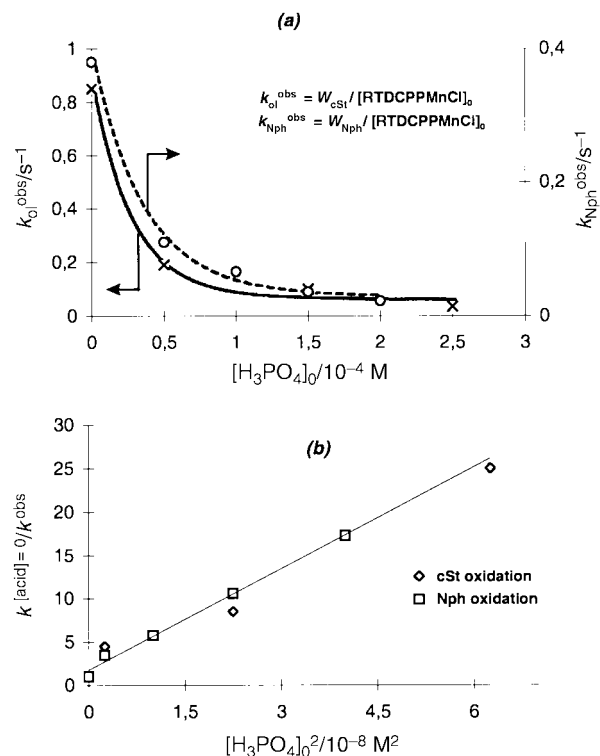


Fig. 5 (a) Dependence of naphthalene (W_{Nph}) and *cis*-stilbene (W_{ol}) oxidation rates on the concentration of H₃PO₄ in reactions catalysed by **2**. [2]₀ = $(1-5) \times 10^{-5}$ M, [Nph]₀ or [cSt]₀ = 0.01 M, [AcOOH]₀ = 0.025–0.05 M, [AcOH]₀ = 0.5 M. (b) Linearization of curves (a).

results obtained with *p*-nitrobenzoic and trichloroacetic acids might be explained by the formation of monoadducts [RTDCPPMn(L)](X) (L = NBA or TCA) showing K_1 and k_2 values different from those of [RTDCPPMn(AcOH)](X).[‡] For L = NBA k_2 may be higher than k_2 for L = AcOH, and specific acidic catalysis is observed in this case (Table 2, lines 6,7).

The present data indicate that the stage of high-valent oxometal species formation does not undergo general acid catalysis. A specific interaction of AcOH with PorMnX takes place instead. The study of the influence of different acids on the oxidation rates of *cis*-stilbene and naphthalene gives another interesting hint. Among the acids tested none provides an oxidation rate dependence on [acid]₀^{0.5} which is typical for an equilibrium proton shifting in aprotic polar solvents such as CH₃CN (equilibrium (c), Scheme 1). However, this is not conclusive with respect to the problem of the possible formation of manganese-peroxoacetate 'A⁻' by dissociation of the adduct 'A'. Indeed, specific AcOH interactions with RTDCPPMnX and with other intermediate species could mask the shift of equilibrium (c) expected in the presence of stronger acids. As mentioned above, the [AcOH]₀ range in which DPPH oxidation rates do not depend on [AcOH]₀ ($0.01 \leq [\text{AcOH}]_0 \leq 0.1$ M) is too narrow to reject the dissociation stage from Scheme 1. Further information on this point was obtained using a scavenger for intermediate 'A' (or 'A⁻') which is less sensitive than DPPH to AcOH, namely the Zn complex of tetra-*tert*-butylphthalocyanine (PcZn).

One-electron oxidation of PcZn

Preliminary UV-Vis studies showed that PcZn does not form aggregates when dissolved in CH₃CN at 10^{-5} – 10^{-4} M concentrations. The UV-Vis spectra of these solutions were independent of [AcOH]₀ up to 0.4 M, thus considerably widening the concentration range for which the dependence of the oxidation rate on [AcOH]₀ can be studied. In the presence of catalysts **1–5**

[‡] For the use of notations K_1 and k_2 see Part 1 and Scheme 1.

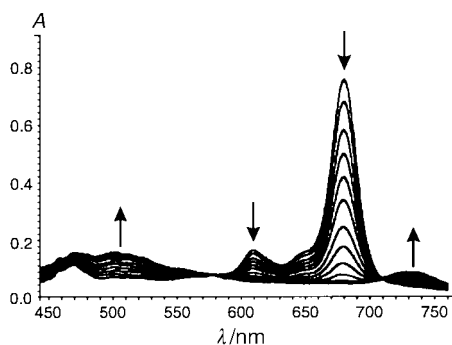


Fig. 6 Difference UV-Vis spectra (absorbance of the solution at time τ – absorbance of the solution at $t = 0$) of the reaction solution in PcZn oxidation with AcOOH catalysed by **2**. $[2]_0 = 1 \times 10^{-6}$ M, $[\text{PcZn}]_0 = 3.5 \times 10^{-6}$ M ($\epsilon_{674 \text{ nm}} = 2.2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), $[\text{AcOOH}]_0 = 9.5 \times 10^{-5}$ M, $[\text{AcOH}]_0 = 0.05$ M. Time intervals = 5 s, $l = 1$ cm.

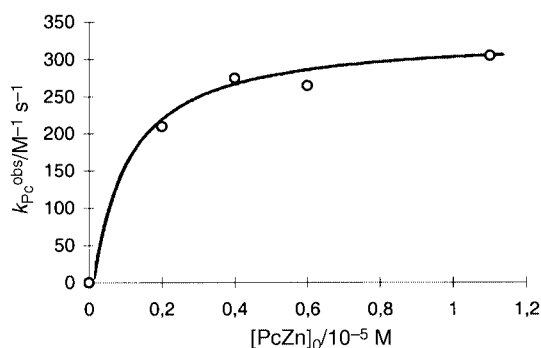
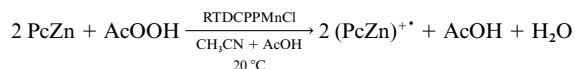


Fig. 7 Dependence of PcZn bleaching rate constant ($k_{\text{pc}}^{\text{obs}}$) on $[\text{PcZn}]_0$ in reactions catalysed by **5**: $[\text{S}]_0 = 0.5 \times 10^{-6}$ M, $[\text{AcOOH}]_0 = 0.95 \times 10^{-4}$ M, $[\text{AcOH}]_0 = 0.025$ M.

PcZn was completely oxidized by AcOOH affording the corresponding stable π -radical cation $(\text{PcZn})^{+\cdot}$, $\lambda_{\text{max}} = 510, 725$ nm (Table 1).³ The reaction stoichiometry (Scheme 4) was



Scheme 4

calculated as $[\text{PcZn}]_{\text{reacted}}/[\text{AcOOH}]_0 = 1.93$ using $[2]_0 = 1 \times 10^{-5}$ M, $[\text{AcOOH}]_0 = 1.4 \times 10^{-5}$ M, $[\text{PcZn}]_0 = 3.5 \times 10^{-5}$ M, $[\text{AcOH}]_0 = 0.05$ M. As verified in the one-electron oxidation of DPPH, UV-Vis spectra of the catalysts did not change in the course of the reaction. The disappearance of PcZn and formation of $(\text{PcZn})^{+\cdot}$ were easily followed by difference UV-Vis spectroscopy (Fig. 6). The rate of PcZn bleaching (W_{pc}) was found to be first order both in $[\text{RTDCPPMnX}]_0$ and $[\text{AcOOH}]_0$, furthermore it exhibits a Michaelis-Menten type dependence on $[\text{PcZn}]_0$ (Fig. 7). W_{pc} independence of both $[\text{PcZn}]_0$ (at $[\text{PcZn}]_0 > 1 \times 10^{-5}$ M) and $[\text{PcZn}]_t$ showed that PcZn, like DPPH, acts as a scavenger for intermediate 'A' (or 'A⁻'). Therefore, the overall process outlined in Scheme 3 for DPPH applies also to the one-electron oxidation of PcZn. Experimental rate constant values k_{pc} for the bleaching of PcZn (eqn. (5)) deter-

$$k_{\text{pc}} = W_{\text{pc}} / (2 [\text{RTDCPPMnX}]_0 [\text{AcOOH}]_0) \quad (5)$$

mined at $[\text{PcZn}]_0 \geq 1 \times 10^{-5}$ M are very close to k_{g} values obtained in DPPH oxidation (Table 1), thus indicating that both DPPH and PcZn are oxidized by the same intermediate ('A' or 'A⁻').

As shown in Table 1, independence of k_{pc} values of $[\text{AcOH}]_0$ has been established for $0.01 \leq [\text{AcOH}]_0 \leq 0.4$ M, a range much wider than $0.01 \leq [\text{AcOH}]_0 \leq 0.1$ M for which independence of k_{g} of $[\text{AcOH}]_0$ was previously verified. These experimental data are in agreement with the hypothesis that the molecular adduct

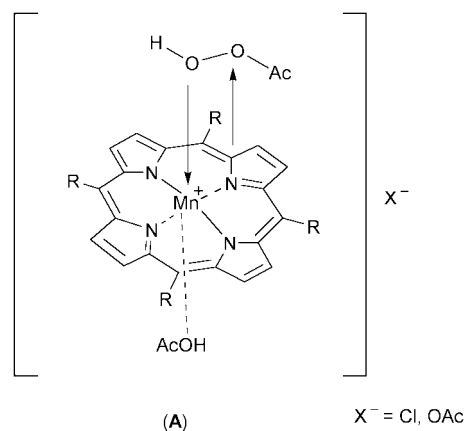


Fig. 8 Proposed structure of molecular adduct 'A'. $X^- = \text{Cl}, \text{OAc}$

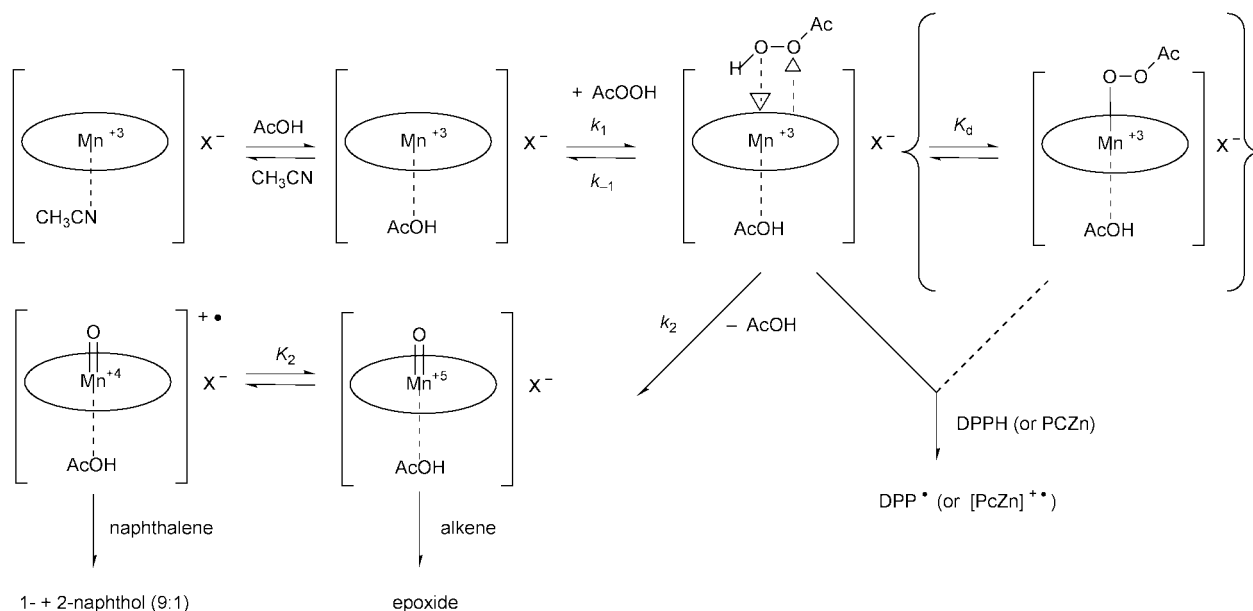
'A' does not dissociate. PcZn (or DPPH) would be therefore oxidized according to path 1 in Scheme 2 and k_{pc} (or k_{g}) would be equal to k_1 in accordance with eqn. (3). It should be pointed out that the alternative path 2, though very unlikely, cannot definitely be ruled out by these kinetic data. Indeed, the acid strength of peracids is greater than that of the corresponding acids.¹⁶ If the dissociation constant of AcOOH does not diminish significantly upon co-ordination with $[\text{RTDCPPMn}(\text{AcOH})](\text{X})$ in adduct 'A', the condition $K_{\text{d}} > K([\text{AcOH}]_0)^{0.5}$ at $[\text{AcOH}]_0$ up to 0.4 M could be attained: k_{pc} (or k_{g}) would therefore be independent of $[\text{AcOH}]_0$ despite eqn. (4), derived from path 2, having to be applied. Nevertheless, bimolecular rate constants for PcZn or DPPH one-electron oxidation, determined in the range of $[\text{AcOH}]_0$ for which $W_{\text{pc}(\text{DPPH})}$ is independent of $[\text{AcOH}]_0$, are equal to the elementary rate constants of $[\text{RTDCPPMn}(\text{AcOH})](\text{X})$ interaction with peracetic acid (k_1 , Table 1), irrespective of the reaction path truly involved.[§]

Influence of peripheral porphyrin substituents on the formation of adduct 'A' and on its transformation into high-valent oxomanganese species

The influence of porphyrin substituents on the generation of oxidizing species in the presence of peracids has been documented in PorFe^{III} catalysed oxidations.¹⁸ On the other hand, similar studies for PorMn^{III} catalysed oxidations have not been reported. Relevant data are here presented for the first time, together with a tentative interpretation of the role played by the porphyrin substituents in PorMn^{III} catalysed oxidations with peracids.

Donor-acceptor interactions between Zn and Fe tetra-*tert*-butylphthalocyanines with benzoyl peroxide had previously been recognized by us, with the donating component (**d**) localized on the macrocycle and the accepting one (**a**) on the central metal ion.¹⁹ Taking into account the common catalytic properties of metallo-porphyrins and their aza analogues, a similar two-component interaction between AcOOH and the Mn-porphyrin in intermediate 'A' (Fig. 8) is conceivable. One of the empty d orbitals of the Mn^{III} ion (d_{z^2} , d_{xz} or d_{yz}) would play the role of accepting site, while the donating component may be localized on one of the α -C pyrrole atoms of the macrocycle, which are included in the HOMO of the metal complexes (two nearly degenerate a_{2u} Gouterman's orbitals).²⁰ As a consequence, the decrease of porphyrin donating ability due to the introduction of electronegative substituents would be balanced by the increase of Mn^{III} accepting properties. Independence of k_1 of the nature of substituents R (Table 1) is in full agreement

[§] Further studies on Mn^{III} tetra-R-tetra-*tert*-butyltetraazaporphines (R = H, Br, PhSO₂ or NO₂), which have catalytic properties close to Mn-porphyrins, but are more sensitive to acidic influence, gave us more indications on this point.¹⁷



Scheme 5

Table 3 Values of k_{ol} , k_{Nph} , K_2 and k_2 determined for *cis*-stilbene and naphthalene oxidation with peracetic acid catalysed by RTDCPPMnCl 1–5 at 20 °C^a

Catalyst	$k_{\text{ol}}/\text{s}^{-1}$	$k_{\text{Nph}}/\text{s}^{-1}$	K_2^b	k_2^c/s^{-1}
1	1.0	0.51	0.51	1.22
2	0.85	0.38	0.44	1.51
3	1.8	0.94	0.52	2.74
4	2.0	0.85	0.42	2.84
5	4.3	3.65	0.85	7.96

^a Reaction conditions: see Table 1, ref. 1; $[\text{AcOH}]_0 : [\text{RTDCPPMnCl}]_0 \geq 1000 : 1$. ^b $K_2 = k_{\text{Nph}}/k_{\text{ol}}$. ^c $k_2 = k_{\text{ol}}(1 + K_2)$.

with this view, so we suggest that the macrocyclic ligand and the central metal ion participate to the same extent in the formation of 'A' upon interaction of $[\text{RTDCPPMn}(\text{AcOH})](\text{X})$ with peracetic acid. The mechanism of electron transfer from the macrocycle to Mn^{III} , which we determined for Mn^{III} (and Mn^{II}) phthalocyanines,²¹ is thus valid also for Mn^{III} -tetraarylporphyrins; this also explains the slight variation of K_2 (Scheme 1) values upon introduction of porphyrin substituents of different nature (Table 3).

The transformation of RTDCPPMnX into $\text{RTDCPPMn}^{\text{V}}(\text{O})(\text{X})$ and $[\text{RTDCPPMn}^{\text{V}}(\text{O})]^+(\text{X})$ upon interaction with peracetic acid in acetonitrile–acetic acid ($[\text{AcOH}] : [\text{RTDCPPMnX}] \geq 1000 : 1$) is summarized in Scheme 5.

Intermediate 'A' being the most likely precursor of the high-valent oxomanganese species, the equilibrium constant K_2 can be calculated for each catalyst using k_{ol} and k_{Nph} values obtained in *cis*-stilbene and naphthalene oxidation experiments (Table 3).¹ One can thus cope with the critical point of the determination of k_2 and its dependence on the catalyst structure. Considering catalyst 2 (R = H) as the reference, eqn. (6)

$$k_{\text{ol}}^{\text{rel}} = \frac{k_{\text{ol}}^{\text{R}}}{k_{\text{ol}}^{\text{H}}} = \frac{(k'_2)^{\text{R}}(1 + K_2^{\text{H}})K_{\text{d}}^{\text{R}}}{(k'_2)^{\text{H}}(1 + K_2^{\text{R}})K_{\text{d}}^{\text{H}}} \quad (6)$$

and the corresponding eqn. (7) can be derived from eqns. (1) and (2).

$$\log(k'_2)^{\text{rel}} = \log \frac{(k'_2)^{\text{R}}}{(k'_2)^{\text{H}}} = \log k_{\text{ol}}^{\text{rel}} - \log \frac{(1 + K_2^{\text{H}})}{(1 + K_2^{\text{R}})} - \log \frac{K_{\text{d}}^{\text{R}}}{K_{\text{d}}^{\text{H}}} \quad (7)$$

Since dissociation of 'A' was excluded, k_2 must be considered

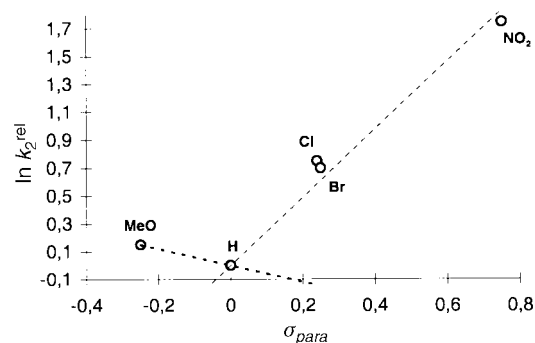


Fig. 9 Hammett-type plot of the dependence of $\text{RTDCPPMn}^{\text{V}}(\text{O})(\text{X})$ formation rate from intermediate 'A' (k_2) on the electronegativity of R substituents (σ_{para}).

instead of k'_2 , the third member of eqn. (7) disappears and the relationship shown in eqn. (8) becomes valid.¶

$$\log k_2^{\text{rel}} = \log k_{\text{ol}}^{\text{rel}} - \log [(1 + K_2^{\text{H}})/(1 + K_2^{\text{R}})] \quad (8)$$

Values of $\log k_2^{\text{rel}}$ can be calculated from the experimental data of Table 3 by using eqn. (8) and plotted against σ_{para} in a Hammett-type correlation (Fig. 9). The non-linear character of this correlation (observed also for Mn^{III} -tetraazaporphines¹⁷) evidenced that both electron donating and electron withdrawing substituents influence the formation of the high-valent oxomanganese species. The efficiency of 'A' transformation into the high-valent oxomanganese species depends on the degree of polarization of the O–O bond, which may be enhanced in a non-compensated mode by the porphyrin donating ability (increased by electron donating substituents) and by increase of the Mn^{III} accepting properties due to introduction of electron-withdrawing substituents on the macrocycle.

Conclusion

New details on the mechanism of RTDCPPMnX interactions with peracetic acid and the nature of the intermediates involved

¶ It should be noted that in the case of Mn^{III} complexes of tetra-*R*-tetra-*tert*-butyltetraazaporphines, adduct 'A' undergoes dissociation.¹⁷ However, K_{d} for this equilibrium is insensitive to the nature of the R substituent in comparison with k_{ol} . By analogy, even if dissociation of 'A' is involved in the mechanism of Mn -porphyrin catalysed oxidation, the third term of eqn. (7) should be negligible.

in oxidation reactions catalysed by these complexes were obtained. UV–Vis spectroscopy showed that Mn^{III}–porphyrins aggregate in pure acetonitrile solutions; aggregation is disrupted when [AcOH]:[RTDCPPMnX] ≥ 1000:1. An adduct [RTDCPPMn(AcOH)](X) is then formed with the inclusion of acetic acid in the internal co-ordination sphere and displacement of the counter anion X to the outer co-ordination sphere of the complex. Donor–acceptor interactions localized on the macrocyclic ligand and on the central Mn^{III} ion respectively rule the formation of intermediate ‘A’ from [RTDCPPMn(AcOH)](X) and AcOOH. Accordingly, the elementary rate constant for ‘A’ formation (k_1) was found to be independent of the nature of the substituents on the porphyrin ring, evidencing full compensation of donor and acceptor components in this stage of the reaction. On the basis of the reasonable assumption that the Mn–peroxoacetate species ‘A[−]’ (Scheme 1) is not involved in the reaction, the elementary rate constant k_2 for the formation of the high-valent oxomanganese species responsible for the epoxidation of *cis*-stilbene and the hydroxylation of naphthalene could be evaluated for each catalyst from the experimentally found k_{ol} and k_{Nph} values.¹ The relative elementary rate constants $k_2^{rel} = k_2^R/k_2^H$ were thus calculated and the values of $\log k_2^{rel}$ correlated with σ_{para} . Although a non-linear dependence of $\log k_2^{rel}$ on σ_{para} was observed, the presence of electron-withdrawing substituents on the porphyrin effectively enhances the rate of formation of the high-valent oxomanganese species (the rate determining step in *cis*-stilbene and naphthalene oxidation) by increasing the accepting properties of the manganese cation. The optimum catalytic properties of Mn^{III}–tetraarylporphyrins of “the second generation” (*i.e.* featuring electron-withdrawing groups on the *meso*-aryl substituents)²² are thus determined not only by their high stability towards AcOOH, but also by their high k_2 values, in contrast with the trend observed with Fe^{III}–tetraarylporphyrins.¹⁸

Experimental

UV–Visible spectra were recorded on a fiber-optic spectrometer “LESA-5 Biospec”. Naphthalene and *cis*-stilbene (Aldrich) were used as received. 1,1-Diphenyl-2-picrylhydrazine (DPPH) was purified by reprecipitation from benzene solutions upon addition of octane. This procedure was repeated at least three times. Acetonitrile (HPLC grade) was additionally purified by distillation on potassium permanganate, then kept 24 h over CaCl₂ and for 24 h on BaO. Mn–porphyrins 1–5, prepared as described in Ref. 1, were dissolved in CH₃CN by gentle heating (30–40 min, 40–50 °C). Oxidation of *cis*-stilbene and naphthalene was carried out as described in Ref. 1. Solutions of peracetic acid in acetic acid (1.3–1.9 M), obtained as previously reported,²³ were diluted with CH₃CN to give the [AcOOH] required in the experiment. Freshly prepared reagents solutions in CH₃CN were employed throughout this work.

One-electron oxidation of DPPH

The mother solutions of DPPH, RTDCPPMnCl and AcOH in CH₃CN were prepared at concentrations three times those desired in the reaction mixture. For experiments with [AcOH]₀ = [AcOH]_{ox}, pure CH₃CN was used instead of the AcOH solution. A typical procedure is described. In a quartz optical cell ($l = 1$ cm) were added in order: 0.5 ml of a solution of DPPH (0.006 M), 0.5 ml of a solution of AcOH (0.15 M) and 0.5 ml of solution of catalyst 2 (7.5×10^{-6} M). The solution was mixed for 5 min and used as a spectral reference. To an otherwise identical solution containing DPPH, AcOH and 2, 0.1 ml of an AcOH–CH₃CN solution of AcOOH (5.0×10^{-4} M) was quickly added. Difference UV–Vis spectra (see Fig. 1) were recorded every 15 s during 500 s. The initial rate of DPPH

($\epsilon = 1.5 \times 10^4$ M^{−1} cm^{−1} at $\lambda = 535$ nm) formation (W_{DPP}) was calculated over the first 100 s.

One-electron oxidation of PcZn

Reactions were carried out at 20 °C as described for DPPH oxidation and followed by UV–Vis spectroscopy, using pure CH₃CN as a spectral reference. The bleaching of PcZn was monitored at $\lambda = 674$ nm ($\epsilon = 2.2 \times 10^5$ M^{−1} cm^{−1}). Time intervals = 5–10 s, reaction time = 10–15 min.

Acknowledgements

The authors thank Professor E. A. Luk’yanets for helpful discussions and for the generous gift of a sample of Zn–tetra-*tert*-butylphthalocyanine. This work was supported by the Russian Foundation for Fundamental Research (grant 97-03-32327).

References

- Part 1, S. Banfi, M. Cavazzini, G. Pozzi, S. V. Barkanova and O. L. Kaliya, in *J. Chem. Soc., Perkin Trans. 2*, 2000, preceding paper (DOI: 10.1039/a905458h).
- V. I. Gavrilov, L. G. Tomilova, I. V. Shelepin and E. A. Luk’yanets, *Elektrokimiya*, 1979, **15**, 1058.
- S. Banfi, M. Cavazzini, F. Coppa, S. V. Barkanova and O. L. Kaliya, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1577.
- S. V. Vulfson, O. L. Kaliya, O. L. Lebedev and E. A. Luk’yanets, *Zh. Org. Khim.*, 1974, **10**, 1757 and references cited therein.
- E. Guilmet and B. Meunier, *Tetrahedron Lett.*, 1982, 2449.
- F. Montanari, M. Penso, S. Quici and P. Viganò, *J. Org. Chem.*, 1985, **50**, 4888; S. Banfi, F. Montanari and S. Quici, *J. Org. Chem.*, 1989, **54**, 1850; F. Montanari, S. Banfi and S. Quici, *Pure Appl. Chem.*, 1989, **61**, 1631.
- A. M. D’A. R. Gonsalves, M. M. Pereira and A. C. Serra, *Ann. Quim. Int. Ed.*, 1996, **92**, 375.
- (a) T. Murakami, K. Yamaguchi, Y. Watanabe and I. Morishima, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1343; (b) Y. Urano, T. Higuchi, M. Hirobe and T. Nagano, *J. Am. Chem. Soc.*, 1997, **119**, 12008.
- O. Almarsson and T. C. Bruice, *J. Am. Chem. Soc.*, 1995, **117**, 4533.
- A. M. D’A. R. Gonsalves and M. M. Pereira, *J. Mol. Catal.*, 1996, **113**, 209 and references cited therein.
- K. R. Rodgers and H. M. Golf, *J. Am. Chem. Soc.*, 1988, **110**, 7049.
- F. D’Souza, G. R. Deviprasad and M. E. Zandler, *J. Chem. Soc., Dalton Trans.*, 1997, 3699; K. Kano, T. Nakayama, M. Takeji and S. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1281; L. L. Shipman, T. M. Cotton, J. R. Norris and J. J. Katz, *J. Am. Chem. Soc.*, 1976, **98**, 8222; R. F. Pasternack, P. R. Huber, P. Boyd, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G. C. Venturo and L. DeC. Hinds, *J. Am. Chem. Soc.*, 1972, **94**, 4511.
- R. D. Arasasingham and T. C. Bruice, *Inorg. Chem.*, 1990, **29**, 1422.
- P. L. Anelli, S. Banfi, F. Legramandi, F. Montanari, G. Pozzi and S. Quici, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1345 and references cited therein.
- R. F. Pasternack, N. Sutin and D. H. Turner, *J. Am. Chem. Soc.*, 1976, **98**, 1908.
- R. C. Blake and M. J. Coon, *J. Biol. Chem.*, 1980, **255**, 4100.
- S. V. Barkanova, E. A. Makarova, O. L. Kaliya and E. A. Luk’yanets, unpublished results.
- K. Yamaguchi, Y. Watanabe and I. Morishima, *J. Am. Chem. Soc.*, 1993, **115**, 4058.
- N. I. Bundina, O. L. Kaliya and O. L. Lebedev, *Zh. Org. Khim.*, 1978, **14**, 2447; Yu. M. Golub, S. V. Barkanova, O. L. Kaliya and O. L. Lebedev, *Zh. Org. Khim.*, 1979, **15**, 1723; S. V. Barkanova, V. M. Derkacheva, O. L. Kaliya and E. A. Luk’yanets, *Zh. Org. Khim.*, 1988, **58**, 1415.
- M. Huber and M. Fuhs, *Ber. Bunsenges. Phys. Chem.*, 1996, **100**, 2057.
- O. V. Dolotova, N. I. Bundina, O. L. Kaliya and E. A. Luk’yanets, *J. Porph. Phthal.*, 1997, **1**, 355.
- D. Dolphin, T. D. Traylor and L. Y. Xie, *Acc. Chem. Res.*, 1997, **30**, 251 and references cited therein.
- S. Banfi, F. Montanari, S. Quici, S. V. Barkanova, O. L. Kaliya, V. N. Kopranchikov and E. A. Luk’yanets, *Tetrahedron Lett.*, 1995, **36**, 2317.

Paper a907134b