Manganese-porphyrins and -azaporphyrins as catalysts in alkene epoxidations with peracetic acid. Part 2. Kinetics and mechanism[1]

Stefano Banfi,*,[a] Marco Cavazzini,[a] Fausta Coppa,[a] Svetlana V. Barkanova*,[b] and Oleg L. Kaliya[b]

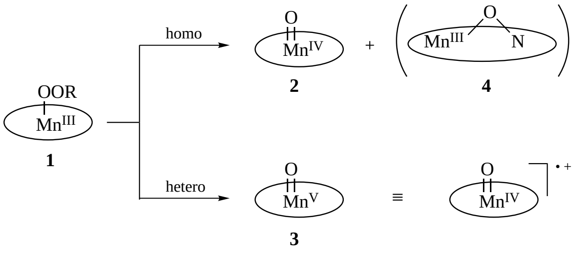
[a] *Centro CNR Studio per la Sintesi e Stereochimica di Speciali Sistemi Organici,*
Via C. Golgi 19, 20135 Milano, Italy
[b] *Organic Intermediates and Dyes Institute, B. Sadovaya 1/4, 103787 Moscow, Russia*

***cis*-Stilbene (cSt) and 1,1-diphenyl-2-picrylhydrazine (DPPH) were used as substrates for kinetic investigations of the catalytic system based on Mn^{III}-porphyrins and peracetic acid in CH_3CN. Catalysts employed were tetra-(2,6-dichlorophenyl)-porphyrinatomanganese chloride (TDCPPMnCl) 5, octanitrophthalocyaninatomanganese chloride ($NO_2PcMnCl$) 6 and tetra(*tert*-butyl)-tetraazaporphyrinatomanganese chloride (TAPMnCl) 7. It was found that for all these catalysts the first step of the reaction mechanism is the formation of an adduct 'A' between the catalyst and AcOOH in a reversible way (k_1/k_{-1}), followed by an irreversible stage (k_2) for the formation of Mn^V-oxo species. The oxidative capability of the adduct 'A' was found to be dependent on the electronic structure of the catalyst, while the reactivity of Mn-oxo species is only slightly influenced by catalyst structure. The formation of the high-valent Mn-oxo species is the rate-determining step of alkene epoxidations as demonstrated by the same k_2 value obtained with catalyst 6 in the epoxidation of cSt and *trans*-stilbene (tSt). Catalyst stability was found to be dependent on solvent polarity, CH_3CN being the best reaction medium.**

In the last fifteen years metallo-complexes of tetraarylporphyrins, phthalocyanines and related macrocycles have been widely studied as catalysts in hydrocarbon oxidations under various conditions.[2] The common factor in these reactions is the formation of a high valent oxometallo intermediate through the reaction of an oxygen donor (OD) with the metal coordinated in the macrocycle centre. This oxo-species is undetectable under the conditions usually employed for oxidations, but it can be isolated at low temperature.[3]

Independent of the nature of the investigated oxidants, the main debate concerns the structure of the high-valent oxometallo species generated by the reaction of the OD with M^{III}-porphyrins and the mechanism of oxygen transfer from metallo-oxo species to the substrate. It is now generally accepted that in the case of Mn^{III}- or Fe^{III}-porphyrins two intermediates, namely $[(P)M^V(O)](X)$ or $[(P)M^{IV}(O)]$, can be formed depending on the reaction conditions.

A variety of mechanisms has been proposed for oxygen transfer, in which intermediates such as metallaoxetane, π-radical cation, carbocation, radical and concerted additions have been recognized.[4] In the case of Fe^{III}-porphyrin, Bruice proposed that all these intermediates could be generated from the evolution of an initial charge transfer complex; however only a concerted mechanism is in accord with the experimental evidence.[4a] In the particular case of hydrocarbon oxidations catalysed by Mn-porphyrins and promoted by alkyl or acyl peroxides (ROOH) two possible pathways have been envisaged for the formation of the metallo-oxo species: the heterolytic or the homolytic cleavage of the O–O bond in the (P)Mn–O–OR intermediate **1**. The mechanism of this step has been investigated in depth by Groves,[3,5a] Morishima,[5b,c] Traylor[5d,e] and Bruice[4a,5f] who independently recognized some general factors influencing the reaction outcome. These factors can be summarized as follows: (*i*) the heterolytic cleavage of **1** is favoured by the presence of acid or by a general hydrogen bonding catalysis;[5a,c] (*ii*) the homolytic cleavage of **1** occurs under basic conditions or in the presence of an electron-donating group coordinated to the metal;[3] (*iii*) from intermediate **1**, homolysis produces an oxomanganese(IV) complex (**2**) , while *via* heterolysis an oxomanganese(V) complex (**3**) becomes the actual oxidizing species; (*iv*) electron-donating substituents of acyl peroxides favour the homolytic cleavage and, *vice versa*, electron-withdrawing substituents increase the heterolytic pathway.[5a,10a] Indeed, *ab initio* as well as semiempirical calculations favour the formation of a third species **4** for both oxoiron and oxomanganese porphyrins, in which the oxygen atom bridges a metal–nitrogen bond;[6] however, this species seems to be unreactive (Scheme 1).[5a,i]

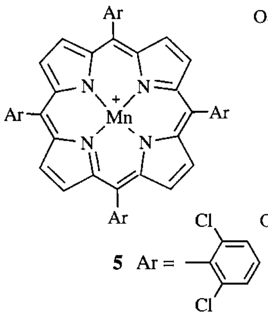


Scheme 1

Furthermore, some peculiar aspects of the formation and reactivity of high valent oxometallo porphyrins were found by each author; an important outcome indicated by Groves concerns the reactivity of $Mn^V{=}O$ species **3** which was found to be stereospecific in *cis*-alkenes epoxidations, while $Mn^{IV}{=}O$ **2** gives both the epoxide isomers.[3]

Despite the enormous amount of work on the mechanism of formation of the oxometallo species and on its reactivity, little attention has been given to the first step of the reaction, *i.e.* the coordination of ROOH to the metal centred inside the porphyrin macrocycle, and to the oxidizing capability of this intermediate. In the last few years, Morishima *et al.* have investigated the reactivity of acyl peroxides with Fe^{III}-porphyrins,[5b,c,g,h] coming to the conclusion that heterolytic cleavage of intermediates like **1** gives the oxo-ferryl porphyrin π-radical-cation $[(P)Fe^{IV}{=}O]^{\bullet +}$ as stereoselective oxidant; in a recent paper they found that the acylperoxo-Fe^{III}-porphyrin adduct (**1**-like) is capable of alkene epoxidations only in apolar solvents, with a stereoselectivity which depends on the peracid structure.[5i] The formation of high valent oxomanganese species through an acylperoxo derivative which was generated by the action of CO_2 on a Mn^{II}-superoxo intermediate was also reported.[6c]

In our previous communication, we compared the catalytic activity of Mn^{III}-porphyrins and Mn^{III}-azaporphyrins in olefin epoxidations, carried out in acetonitrile at 20 °C by using a stoichiometric amount, with respect to the alkene, of peracetic acid (AcOOH) as oxygen donor.[1] With an alkene/catalyst ratio up to 3600, *cis*-stilbene (cSt) oxidation occurs quantitatively and stereospecifically to give the corresponding epoxide in *ca.* 1 h; the non-catalysed reaction is hampered by keeping the peracid initial concentration below 0.1 M. The reaction stereospecificity favours a direct insertion of oxygen from the high-valent metallo-oxo species **3** into the alkene double bond; however, from previous studies carried out on azaporphyrins and peroxo oxidants, we had evidence that an intermediate, formed by coordination of the oxidant to the metallo macrocycle, could be the effective oxidant.[7a] Bruice came to similar conclusions from computer simulation of the time courses of oxidant disappearance and epoxide formation in the Mn^{III}-porphyrin–*p*-cyano-*N*,*N*-dimethylaniline-*N*-oxide system.[7b] The unusually high efficiency of *cis*-stilbene epoxidation featured by the Mn-porphyrin–peracetic acid system prompted us to investigate in more detail the reaction mechanism; in particular we wish to understand, by means of kinetic measurements of two different reactions (epoxidation and one electron oxidation), whether the coordination of peracetic acid to Mn-porphinoids [tetra-(2,6-dichlorophenyl)porphyrinatomanganese chloride (TDCPPMnCl) **5**, octanitrophthalocyaninatomanganese chloride (NO_2PcMnCl) **6** and tetra(*tert*-butyl)-tetraazaporphyrinatomanganese chloride (TAPMnCl) **7**] leads to intermediate **1** featuring specific oxidative capability.



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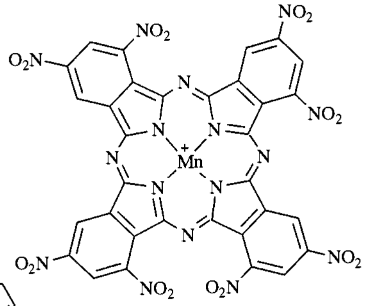

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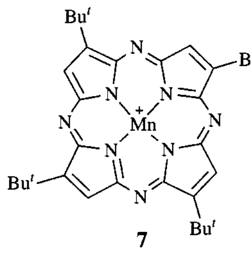

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In order to get reliable values of elementary rate constants, it must be established if the coordination of OD with metalloporphyrins occurs *via* a reversible or an irreversible stage. Furthermore, the comparison between the kinetic constant values of three structurally different catalysts, such as **5**–**7**, gives the extent of the influence of the manganese electronic environment on reaction mechanism. These values can be used for the correlation between catalyst reactivities and structures, then to find out the requirements for a high catalytic activity.

Experimental

GC analyses were performed using internal standard method (standard = *ortho*-dichlorobenzene) on a Hewlett Packard 5890 model, equipped with an OV-1 (15 m × 0.2 mm, 0.5 µm) or a RSL-200 (HP5 type) (30 m × 0.53 mm, 1.2 µm) column. The injector temperature was set at 150 °C, while the detector (FID) was kept at 300 °C. *cis*-Stilbene (cSt), *trans*-stilbene (tSt), *cis*-stilbene epoxide (cStO), *trans*-stilbene epoxide (tStO) and 1,1-diphenyl-2-picryl-hydrazine (DPPH) were commercial products and were used as received. Tetra-(2,6-dichlorophenyl)porphyrinatomanganese chloride (TDCPPMnCl) **5**,[2c] octanitrophthalocyaninatomanganese chloride (NO_2PcMnCl) **6** and tetra(*tert*-butyl)tetraazaporphyrinatomanganese chloride (TAPMnCl) **7**[8] were synthesized following known procedures; CH_3CN and CH_2Cl_2 were Baker HPLC grade solvents.

Peracetic acid (AcOOH) in acetic acid (1.2–1.7 M) was prepared from 30% H_2O_2 and acetic anhydride as described in ref. 1 and its molarity was measured by iodometric titration just before use. The absence of free H_2O_2 was confirmed by $KMnO_4$ (0.01 M) titration at 0 °C. UV–VIS spectra were recorded with a Perkin-Elmer Lambda 6 spectrophotometer, thermostatted at 20 °C.

General method for cSt and tSt epoxidation

In a round-bottomed flask were added in order: 1.0 ml of a CH_3CN solution (0.025 M) of the alkene, 2.0 ml of a CH_3CN solution (0.0125 M) of standard, 1.5 ml of a CH_3CN solution (6.7×10^{-6} M) of the desired catalyst and, finally, the required amount of AcOOH to achieve the desired ratio with respect to the alkene (see text). A total volume of 5 ml was always ensured. The mixture was stirred and samples of 200 µl were withdrawn at fixed times, treated with a saturated aqueous thiosulfate (1 ml) and extracted with 1 ml of Et_2O; the organic layer was then dried ($MgSO_4$) and analysed by GC. cSt disappearance and cStO formation with catalysts **5**–**7** are reported in Fig. 1(*a*–*c*), while the results of tSt oxidation with **6** are reported in Fig. 3(*a*). The dependence of initial rate of cSt epoxidation on peracetic acid initial concentration $[AcOOH]_0$ is reported in Fig. 3(*b*).

General method for DPPH oxidation

Into quartz cells were added 1 ml of a CH_3CN solution (6.0×10^{-3} M) of 1,1-diphenyl-2-picrylhydrazine (DPPH) and 1 ml of a CH_3CN solution (3.0×10^{-5} M) of Mn-catalyst **5**–**7**. Then the reference cuvette was filled with 1 ml of CH_3CN, while 1 ml of a freshly prepared CH_3CN solution of peracetic acid (1.5×10^{-5} M) was added in the analysis cuvette and rapidly shaken. The absorbance increase at 525 nm ($\varepsilon = 1.5 \times 10^4$ dm^3 mol^{-1} cm^{-1}) was detected every 10 s.

DPPH oxidation in the presence of cSt

Following the general procedure described for DPPH oxidation, the initial rates were monitored in the presence of different initial concentrations of cSt ($[cSt]_0$). To this end, CH_3CN solutions of DPPH [3.0 (or 6.0) × 10^{-3} M] were prepared, containing the desired ratio of cSt. The results are reported in Fig. 4(*a*–*c*).

UV–VIS analyses of catalyst (5–7) stabilities in the presence of AcOOH

Into a quartz cell containing 2.3 ml of a CH_3CN solution (2.0×10^{-5} M) of Mn-catalyst were added 0.2 ml of a CH_3CN solution (0.115 M) of peracetic acid, obtained by dilution of the acetic acid mother solution. The mixture was rapidly shaken and analysed between 350–600 nm, with a scan interval of 30 s. As an example, spectral changes of Mn-porphyrin **5** (in CH_3CN) are reported in Fig. 6, while the behaviour of a 0.7×10^{-5} M solution of **5** in CH_2Cl_2 is shown in Fig. 5. In the particular case of the formation of stable species (λ_{max} 415 nm) by the action of peracetic acid on catalyst **5** in CH_3CN, cSt (7 µl of a 0.5 M solution) was added to the sample and the reappearance of the Mn^{III}-porphyrin Soret band at 474 nm was observed (Fig. 7).

Results and discussion

To determine the formation and the reactivity of a metalloporphyrin–peracetic acid intermediate of coordination (molecular complex), prior to the formation of manganese-oxo species, we have studied the kinetic behaviour of two well known model reactions[9,12] in the presence of catalysts **5**–**7**: *cis*-stilbene (cSt) epoxidation and 1,1-diphenyl-2-picrylhydrazine (DPPH) one electron oxidation. cSt was considered as the model substrate because the high valent oxomanganese complexes easily transfer oxygen to this substrate to give the *cis*- or *trans*-epoxide and few other byproducts of rearrangement; the reaction stereoselectivity can be easily correlated to the nature of the oxomanganese species involved. On the other hand, DPPH reacts with any oxidative species able to undergo electron transfer reaction to give the extremely stable radical DPPHyl; then DPPH may be used as a trap for either oxomanganese species **3** or Mn-peroxoacetate **1**. (Species **2** is not envisaged because, as said above, its formation is not allowed under acidic conditions.)

Kinetics of *cis*-stilbene (cSt) oxidation with AcOOH catalysed by TDCPPMnCl 5

cis-Stilbene oxidation was carried out with AcOOH and catalyst **5** in CH_3CN at 20 °C. *cis*-Stilbene epoxide (cStO) and cSt concentrations were measured by GC. Kinetic measurements of cSt disappearance and cStO formation were fulfilled in the following initial concentration ranges: $[\mathrm{TDCPPMnCl}]_0 = 0.8$–$3.6 \times 10^{-6}$, $[\mathrm{cSt}]_0 = 0.25$–1×10^{-2} and $[\mathrm{AcOOH}]_0 = 0.25$–$1 \times 10^{-1}$ M. Higher peracid concentrations give uncatalysed oxidations to a high degree, accompanied by a more prominent catalyst destruction, probably related to the side formation of acyloxyl radicals. For all reagent concentrations used, kinetic curves of cSt consumption obey a zero-order reaction law, with respect to [cSt], up to more than 80% of cSt conversion. The rate of cSt consumption (W_{cSt}) was also independent of $[\mathrm{AcOOH}]_0$ and first order in $[\mathrm{TDCPPMnCl}]_0$. It must be pointed out that this catalyst is particularly robust, being able to reach several thousand turnovers,[1] then its degradation is negligible during the kinetic study; finally the rate of cStO formation (W_{cStO}) was shown to be equal to W_{cSt} [Fig. 1(*a*)]. These results allow us to conclude that in the chosen catalytic system, the rate of olefin disappearance is equal to rate of $[\mathrm{TDCPPMn^V(O)X}]$ **3** formation [eqn. (1)].

$$W_{[\mathrm{TDCPPMn^V(O)X}]} = W_{\mathrm{cSt}} = W_{\mathrm{cStO}} = k_{\mathrm{obs}}\,[\mathrm{TDCPPMnCl}]_0 \qquad (1)$$
$$k_{\mathrm{obs}} = 0.75\ \mathrm{s}^{-1}$$

The presence of an oxomanganese(V) species, instead of an oxomanganese(IV), is supported by literature data for heterolytic cleavage of the adduct '**A**' under acidic catalysis and confirmed by the complete stereoselectivity of epoxide formation.[3,5]

Independence of reaction rate on $[\mathrm{AcOOH}]_0$ indicates strongly that (*i*) the reaction under study occurs through the formation of an intermediate (complex '**A**') which is the oxomanganese(V) precursor; (*ii*) complex '**A**' must be formed in a *reversible stage*; indeed, supposing that '**A**' is generated through an irreversible stage, the rate of its formation should have a linear dependence on $[\mathrm{AcOOH}]_0$.

On the other hand, independence of reaction rates on $[\mathrm{cSt}]_0$ and $[\mathrm{cSt}]_t$ proves that $\mathrm{TDCPPMn^V(O)X}$ formation occurs in an irreversible stage from intermediate '**A**'. This adduct may be envisaged as a molecular complex between the catalyst and the oxidant [(P)MnX···HOOAc] or as a peracetate manganese salt [(P)Mn–OOAc]. Complexes of Mn- and Fe-porphyrins with $ArCO_3H$ similar to the latter were proposed as a source of corresponding oxo-complexes.[5i,10]

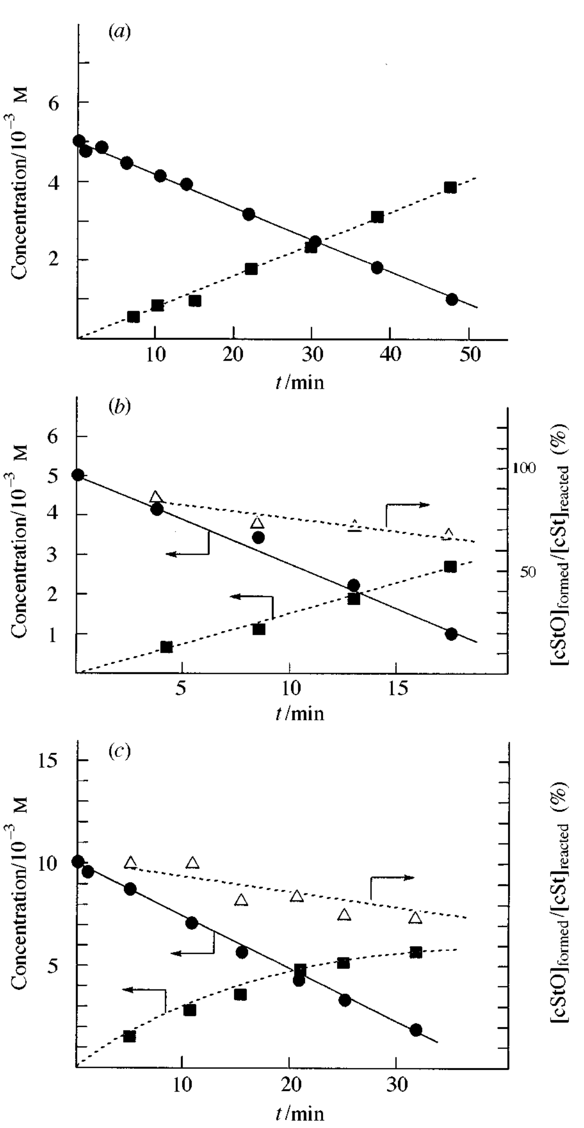

Fig. 1 (*a*) Kinetics curves of cSt conversions (●) and cStO formation (■) for the reaction catalysed by TDCPPMnCl (**5**); $[\mathbf{5}]_0 = 1.8 \times 10^{-6}$; $[\mathrm{AcOOH}]_0 = 0.054$ M; CH_3CN, 20 °C. (*b*) Kinetic curves of cSt conversion (●), cStO formation (■) and $[\mathrm{cStO}]_{\mathrm{formed}}/[\mathrm{cSt}]_{\mathrm{reacted}}$% ratio (△) for the reaction catalysed by $NO_2PcMnCl$ (**6**): $[\mathbf{6}]_0 = 1.85 \times 10^{-6}$; $[\mathrm{AcOOH}]_0 = 0.087$ M; CH_3CN, 20 °C. (*c*) Kinetic curves of cSt conversion (●), cStO formation (■) and $[\mathrm{cStO}]_{\mathrm{formed}}/[\mathrm{cSt}]_{\mathrm{reacted}}$% ratio (△) for the reaction catalysed by TAPMnCl (**7**): $[\mathbf{7}]_0 = 1.6 \times 10^{-6}$; $[\mathrm{AcOOH}]_0 = 0.027$ M; CH_3CN, 20 °C.

According to these observations the mechanism of $\mathrm{TDCPPMn^V(O)X}$ formation as well as cSt oxidation can be represented by Scheme 2.

$$\mathrm{TDCPPMnX} + \mathrm{AcOOH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{'}\mathbf{A}\text{'}$$
$$\text{'}\mathbf{A}\text{'} \xrightarrow{k_2} [\mathrm{TDCPPMn(O)X}] + \mathrm{AcOH}$$
$$[\mathrm{TDCPPMn(O)X}] + \mathrm{cSt} \xrightarrow{k_3} \mathrm{cStO} + \mathrm{TDCPPMnX}$$

Scheme 2

In the case of $\mathrm{TMPFe^{III}X}$ interaction with aryl peracids it was established that the transformation of its peroxo-complex to the corresponding oxene is catalysed by acid.[5a] Under the reaction conditions used for the kinetic study on cSt epoxidation (tenfold excess of peracid with respect to the substrate) we found that the rate of epoxidation catalysed by **5** was independent of $[\mathrm{AcOH}]_0$ in the range 0.18–1.8 M, the acid concentration being much greater than that of the catalyst.

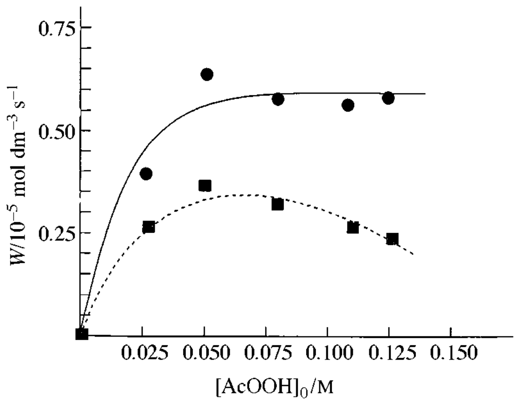

Fig. 2 Dependence of W_{cSt} (●) and W_{cStO} (■) on $[\mathrm{AcOOH}]_0$ for the reaction catalysed by NO_2PcMnCl (**6**): $[\mathbf{6}]_0 = 1.8 \times 10^{-6}$; $[\mathrm{cSt}]_0 = 5 \times 10^{-3}$ M; CH_3CN, 20 °C

From Scheme 2, the rate of TDCPPMn^{V}(O)(X) formation [eqn. (2)], which is equal to W_{cSt} and to W_{cStO}, can be calculated in the frame of *quasi*-steady state approximation. This is

$$W_{[\mathrm{TDCPPMn^V(O)X}]} = \frac{k_1k_2\,[\mathrm{TDCPPMnX}]_0[\mathrm{AcOOH}]_0}{(k_1+k_2)\{1+k_1[\mathrm{AcOOH}]_0/(k_1+k_2)\}} \qquad (2)$$

transformed to eqn. (3) at high $[\mathrm{AcOOH}]_0$ when $\{k_1[\mathrm{AcOOH}]_0/(k_{-1}+k_2)\} \gg 1$. Eqn. (3) is identical to the experimental one

$$W_{[\mathrm{TDCPPMn^V(O)X}]} = k_2\,[\mathrm{TDCPPMnX}]_0 \qquad (3)$$

[eqn. (1)] at $k_2 = k_{\mathrm{obs}} = 0.75$ s^{-1}; k_2 represents the rate constant of the elementary stage of oxomanganese(v) formation. The k_2 values obtained from different catalysts may be used for a useful comparison of catalyst capabilities to form oxomanganese species from the molecular complex intermediates.

Kinetics of *cis*-stilbene oxidation with AcOOH catalysed by octanitrophthalocyaninatomanganese chloride (NO_2PcMnCl) 6 and tetra(*tert*-butyl)-tetraazaporphyrinatomanganese chloride (TAPMnCl) 7

Kinetic measurements of *cis*-stilbene epoxidation in the presence of catalysts **6** and **7** were carried out with the following initial molar ratios: $[\mathbf{6}]_0 = 0.4\text{–}3.7 \times 10^{-6}$ or $[\mathbf{7}]_0 = 0.8\text{–}3.2 \times 10^{-6}$; $[\mathrm{AcOOH}]_0 = 0.25\text{–}1.1 \times 10^{-1}$; $[\mathrm{cSt}]_0 = 0.25\text{–}1.1 \times 10^{-2}$ M. As seen in the case of catalyst **5**, kinetic curves of cSt disappearance obey a zero-order law on $[\mathrm{cSt}]_t$ with catalysts **6** and **7** [Fig. 1(*b*,*c*)]; the rate of cSt oxidation (W_{cSt}) is independent of initial cSt and AcOOH concentrations (at $[\mathrm{AcOOH}]_0 > 0.05$ M as shown in Fig. 2) and W_{cSt} is described by eqn. (1) with $k_{\mathrm{obs}} = 3.5$ and 4.0 s^{-1} for **6** and **7** respectively. These results indicate that the kinetics of cSt disappearance are similar for all Mn-complexes; the catalyst structure then slightly influences the rate of formation of the high valent metallo-oxo species within the complexes investigated.

In the case of **6** the rate of cStO formation (W_{cStO}) is not equal to the rate of cSt disappearance and, although a linear dependence on $[\mathrm{cSt}]_0$ was observed [Fig. 1(*b*)], both W_{cStO} and W_{cSt} show a non-linear dependence on $[\mathrm{AcOOH}]_0$ (Fig. 2). It must be pointed out that by using only a slight excess of peracid with regard to the substrate ($[\mathrm{AcOOH}]_0:[\mathrm{cSt}]_0 = 1.1:1$) the selectivity in cStO formation approaches 100% whichever catalyst is used.[1]

We assume that the lower selectivity observed in the case of catalysts **6** and **7**, under the reaction conditions used for the kinetic studies (ten times excess of oxidant with respect to the alkene), was due to the low stability of these catalysts. Their degradation releases free metal ions which, in turn, could catalyse the peracid radical decomposition; the reactions of these radicals with cSt consume the alkene but do not produce the epoxide. Catalyst stability can be evaluated following the modification of the UV–VIS spectra during the oxidation reactions. In fact the intensity of the Soret band is proportional to catalyst concentration and it is known that the degree of degradation depends on the nature of the oxidant and on the presence of an oxidisable substrate.[2b,11a,b] In order to evaluate if catalyst destruction originated from peracid radical decomposition we have run some spectrophotometric investigations on the behaviour of catalysts **5**–**7** with AcOOH and in the absence of cSt; the results will be reported later.

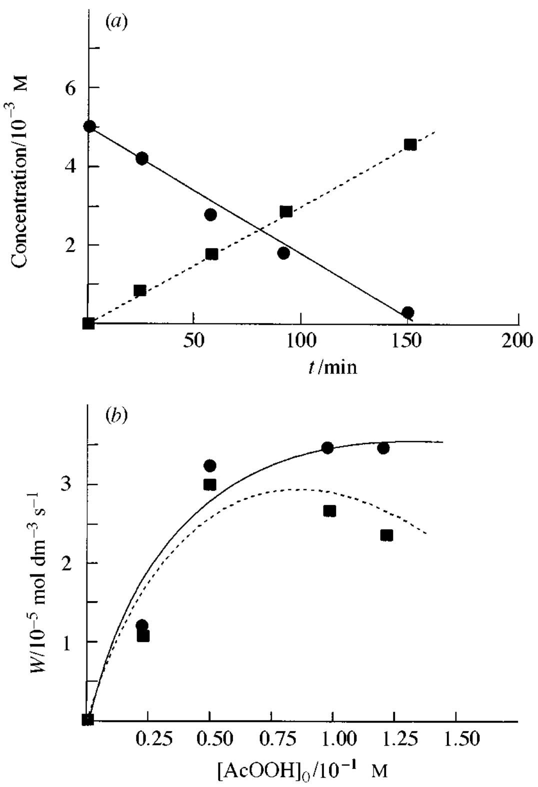

Fig. 3 (*a*) Kinetic curves of tSt conversion (●) and tStO formation (■) for the reaction catalysed by NO_2PcMnCl (**6**): $[\mathbf{6}]_0 = 1.0 \times 10^{-5}$; $[\mathrm{AcOOH}]_0 = 0.05$ M; CH_3CN, 20 °C. (*b*) Dependence of W_{tSt} and W_{tStO} on $[\mathrm{AcOOH}]_0$ for the reaction catalysed by NO_2PcMnCl (**6**): $[\mathbf{6}]_0 = 7 \times 10^{-5}$ M; CH_3CN, 20 °C.

The results of the kinetic studies allow us to hypothesize that, at a given catalyst concentration, the rate of olefin epoxidation should be independent of alkene structure and should only be determined by the rate constant of Mn-oxene formation (k_2). To support this conclusion we have measured k_2 in *trans*-stilbene (tSt) oxidation with AcOOH catalysed by NO_2PcMnCl **6**. This catalyst was chosen because its planar structure allows the formation of the corresponding epoxide (tStO) as a single product (it is well known that the oxomanganese species of sterically hindered tetraarylporphyrin does not transfer the oxygen atom to *trans*-alkenes).[1]

Kinetics of *trans*-stilbene oxidation with AcOOH catalysed by NO_2PcMnCl 6

Oxidation of tSt was carried out at $[\mathbf{6}]_0 = 0.25\text{–}1.0 \times 10^{-5}$; $[\mathrm{AcOOH}]_0 = 0.2\text{–}1.2 \times 10^{-1}$; $[\mathrm{tSt}]_0 = 0.5\text{–}1.0 \times 10^{-2}$ M. As observed in the case of cSt, kinetic curves of tSt disappearance (W_{tSt}) and those of *trans*-stilbene oxide formation (W_{tStO}) obey a zero-order reaction law on $[\mathrm{tSt}]_t$ [Fig. 3(*a*)]; W_{tSt} is described by the experimental eqn. (1) {at $[\mathrm{AcOOH}]_0 > 0.05$ M, Fig 3(*b*)} with $k_{\mathrm{obs}} = 3.3$ s^{-1}.

In contrast with cSt oxidation, the rate values of tStO formation are equal to those of tSt disappearance at AcOOH initial concentrations lower than 0.075 M [Fig. 3(*b*)]; at higher peracid concentrations W_{tStO} values are *ca.* 20% lower than that of W_{tSt}. The comparable k_2 values calculated for both *cis*-

and *trans*-stilbene epoxidations confirm that alkene oxidation rates are independent of substrate structure and support our conclusion about oxomanganese(V) formation in an *irreversible stage*.

Kinetics of DPPH oxidation with AcOOH catalysed by 5–7

Manganese complexes **5**–**7** were used to measure the k_1 values using the method, developed in a previous study, for both metal complexes[12a] and non-metallic[12b] porphyrin-like compounds in the presence of benzoyl peroxide. It was found that molecular complexes of pattern ‘**A**’ can oxidize DPPH, yielding the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPHyl). At high DPPH concentrations, when the rate of DPPH oxidation (or DPPHyl formation) is higher than the sum of the rates of molecular complex dissociation and of its irreversible decomposition ($W_{\mathbf{DPPHyl}}$ is independent of $[\mathrm{DPPH}]_0$), the first stage of interaction between porphyrin-like compounds and oxidant becomes irreversible; hence it is possible to determine the values of the elementary rate constant k_1. On the basis of this knowledge we have studied the kinetics of DPPH oxidation with AcOOH in the presence of catalysts **5**–**7**, confident that their molecular complexes with AcOOH can oxidize DPPH to DPPHyl. Kinetics of DPPHyl formation ($\lambda_{\mathbf{max}}$ 525 nm, $\varepsilon = 1.5 \times 10^4$ dm^3 mol^{-1} cm^{-1}) were studied using $[\mathrm{DPPH}]_0$ in the range 10^{-3}–10^{-2} M and the following catalyst and peracetic acid molar concentrations: $[\mathbf{6}]_0 = 0.25$–1.0×10^{-5}, $[\mathrm{AcOOH}]_0 = 0.2$–0.9×10^{-5}; $[\mathbf{7}]_0 = 2.7$–11×10^{-5}, $[\mathrm{AcOOH}]_0 = 3$–6×10^{-5}; $[\mathbf{5}]_0 = 4$–16×10^{-5}, $[\mathrm{AcOOH}]_0 = 0.18$–$7.8 \times 10^{-5}$ M.

This reaction was studied at $[\mathrm{AcOOH}]_0$ concentration lower than that of the catalyst in order to keep the acid concentration in the reaction medium below 10^{-3} M (the peracid mother solution is in acetic acid); indeed we have found that DPPH oxidation is acid catalysed, and only at low AcOH molarity is the acid catalysed reaction negligible. Under the above mentioned conditions, the experiments have shown the absence of non-catalysed DPPH oxidation. Taking into account the experimentally obtained ratio $[\mathrm{DPPH}]:[\mathrm{AcOOH}]_0 = 2:1$, the whole investigated process may be represented as eqn. (4). The initial

$$\mathrm{AcOOH} + 2\mathrm{DPPH} \xrightarrow{\text{Mn-catalyst}} 2\mathrm{DPPHyl} + \mathrm{H_2O} + \mathrm{AcOH} \qquad (4)$$

rate of DPPHyl formation ($W^{\mathbf{in}}_{\mathbf{DPPHyl}}$) is independent of DPPH concentration, within the range $[\mathrm{DPPH}]_0 = 10^{-3}$–$10^{-2}$ M, and it is described by eqn. (5), where values of $k_{\mathbf{DPPHyl}} = 150$, 3500 and

$$W^{\mathbf{in}}_{\mathbf{DPPHyl}} = k_{\mathbf{DPPHyl}}[\mathrm{PMn(X)}]_0\,[\mathrm{AcOOH}]_0 \qquad (5)$$

96 dm^3 mol^{-1} s^{-1} were found for catalysts **5**, **6** and **7** [indicated as PMn(X)], respectively. According to Scheme 2, DPPH oxidation may occur both by the action of intermediate ‘**A**’ and of the high valent Mn-oxo species and can be represented as in Scheme 3. From this Scheme eqn. (6) for DPPHyl formation

$$\mathrm{PMn(X)} + \mathrm{AcOOH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{‘}\mathbf{A}\text{’}$$

$$\text{‘}\mathbf{A}\text{’} \xrightarrow{k_2} \mathrm{PMn(O)X} + \mathrm{AcOH}$$

$$\text{‘}\mathbf{A}\text{’} + \mathrm{DPPH} \xrightarrow{k_6} \xrightarrow{\mathrm{DPPH}} 2\mathrm{DPPHyl} + \mathrm{AcOH} + \mathrm{H_2O} + \mathrm{PMn(X)}$$

$$\mathrm{PMn(O)X} + \mathrm{DPPH} \xrightarrow{k_7} \xrightarrow{\mathrm{DPPH}} 2\mathrm{DPPHyl} + \mathrm{H_2O} + \mathrm{PMn(X)}$$

Scheme 3

$$W_{\mathbf{DPPHyl}} = \frac{2k_1[\mathrm{PMn(X)}]_0[\mathrm{AcOOH}]_0(k_6[\mathrm{DPPH}]_0 + k_2)}{k_{-1} + k_2 + k_6[\mathrm{DPPH}]_0} \qquad (6)$$

rate ($W_{\mathbf{DPPHyl}}$) can be calculated assuming that at low $[\mathrm{AcOOH}]_0$, $[\mathrm{PMn(X)}]_{\mathbf{free}} = [\mathrm{PMn(X)}]_0$.

Table 1 Rate constants of intermediate ‘**A**’ (k_1) and Mn-oxene (k_2) formation in $\mathrm{CH_3CN}$ at 20 °C

	TDCPPMnCl **5**	$\mathrm{NO_2}$PcMnCl **6**	TAPMnCl **7**
k_1/dm^3 mol^{-1} s^{-1}	75	1750	48
k_2/s^{-1}	0.75	3.5	3.0

Experimentally the observed independence of $W^{\mathbf{in}}_{\mathbf{DPPHyl}}$ on $[\mathrm{DPPH}]_0$ at high $[\mathrm{DPPH}]_0$ shows that all intermediates ‘**A**’ are trapped by DPPH, *i.e.* $k_6[\mathrm{DPPH}]_0 \gg (k_{-1} + k_2)$. In this case eqn. (6) is identical to the experimental one [eqn. (5)] at $k_{\mathbf{DPPHyl}} = 2k_1$, and the $k_1$values 75, 1750 and 48 dm^3 mol^{-1} s^{-1} were found for catalysts **5**, **6**† and **7** respectively. From these values it clearly appears that k_1 is related to the structure of the macrocycle; the different electron-density on the metal, which depends on the presence of electron-withdrawing or electron-donating substituents on the macrocycle periphery, influences molecular complex ‘**A**’ formation and it is reasonable that the reactivity of this adduct is also affected. The comparison of k_1 and k_2 values (Table 1) in relation to catalyst structures suggests strongly that the degree of macrocycle participation in formation of intermediate ‘**A**’ is higher than in formation of oxomanganese complexes.

This fact may be explained by the formation of a doubly coordinated intermediate between Mn-macrocycle and peracetic acid in which both the central metal and one nitrogen atom of the periphery link the same molecule of peracid, as acceptor and donor sites, respectively. A similar complex has already been observed in the reaction of Zn and Fe phthalocyanines with benzoyl peroxide.[12c]

Traylor reported that the mechanism of oxygen transfer from oxometallo porphyrin species to alkene ranges from electrophilic addition to electron transfer.[13] We decided to investigate closely this particular aspect of the Mn-porphyrin catalysed oxidations following the competitive oxidations of DPPH and cSt with the aim of discriminating between the oxidative properties of adduct ‘**A**’ and those of the oxomanganese.

Evaluation of oxomanganese(V) and adduct ‘A’ oxidative properties

According to the reported mechanism, two types of intermediates featuring oxidative properties are formed by the reaction of Mn-porphyrins with peracetic acid: the molecular complex ‘**A**’ and the high valent oxomanganese(V) species. In the case of Fe-porphyrins it was established that epoxide formation from alkenes may be carried out either by oxoiron complexes and by the corresponding peroxo complexes (P)FeOOCOAr, while Groves[10b] reported conversion of cyclooctene to cyclooctene epoxide by TMsPMnOOAc only in 30% yield. In order to compare the reactivity of Mn$^{\mathrm{V}}$-oxene complexes of catalyst **5**–**7** and corresponding molecular adducts ‘**A**’, we have studied the influence of added cSt on DPPH oxidation rate. Indeed, at high $[\mathrm{DPPH}]_0$, when the rate of DPPH oxidation, $W^{\mathbf{in}}_{\mathbf{DPPHyl}}$, is independent of $[\mathrm{DPPH}]_0$, there is no source for formation of oxomanganese(V) complexes. In this case the single complex with oxidative properties which can be formed is the molecular complex ‘**A**’, and, if this complex can oxidize olefins, the rate of DPPHyl formation must decrease on increasing the amount of $[\mathrm{cSt}]_0$ added. In a four-component system (PMnCl+AcOOH + DPPH + cSt) $W^{\mathbf{in}}_{\mathbf{DPPHyl}}$ strongly depends on $[\mathrm{cSt}]_0$ when **5** and **7** are the catalysts, while in the presence of **6** the rate of DPPHyl formation is only slightly reduced. As shown in Fig. 4(*a*–*c*), adding 0.055 M cSt decreases $W^{\mathbf{in}}_{\mathbf{DPPHyl}}$ about ten times for TDCPPMnCl and TAPMnCl and only 1.65 times for $\mathrm{NO_2}$PcMnCl.

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† In the case of **6** the value of $k_1/k_{-1} = K_1$ was found to be 17.4 dm^3 mol^{-1} as calculated from Fig. 2.

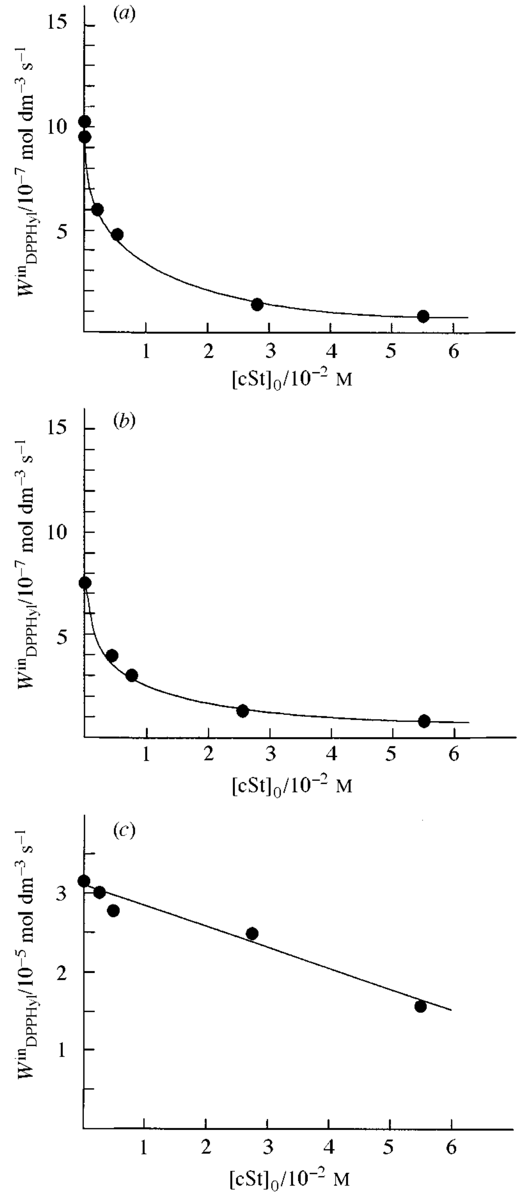

Fig. 4 (*a*) Influence of $[cSt]_0$ on W^{in}_{DPPHyl} catalysed by TDCPPMnCl (**5**); $[\mathbf{5}]_0 = 8 \times 10^{-5}$; $[AcOOH]_0 = 7.8 \times 10^{-5}$; $[DPPH]_0 = 1 \times 10^{-3}$ M. (*b*) Influence of $[cSt]_0$ on W^{in}_{DPPHyl} catalysed by TAPMnCl (**7**); $[\mathbf{7}]_0 = 5.5 \times 10^{-5}$; $[AcOOH]_0 = 5.2 \times 10^{-5}$; $[DPPH]_0 = 2 \times 10^{-3}$ M. (*c*) Influence of $[cSt]_0$ on W^{in}_{DPPHyl} catalysed by NO_2PcMnCl (**6**); $[\mathbf{6}]_0 = 0.92 \times 10^{-5}$; $[AcOOH]_0 = 0.97 \times 10^{-5}$; $[DPPH]_0 = 1 \times 10^{-3}$ M

The different behaviour in electron transfer reaction with DPPH of adduct '**A**' derived from **6** with respect of those from **5** and **7** can be ascribed to its higher electron affinity. The eight nitro groups of the flat phthalocyanine **6** increase the electron deficiency of the metal through both inductive and mesomeric effects. As a consequence cSt epoxidation, which occurs through an electrophilic transfer of the oxygen to the alkene, occurs at a higher rate, as does electron transfer from DPPH, as confirmed by the highest k_2 and k_1 values found for catalyst **6** with respect to **5** and **7**. It has to be noted that k_1/k_2 ratios are 100, 500 and 16 for catalysts **5**, **6** and **7** respectively, thus indicating that the electron deficiency of the macrocycle affects to a greater extent the electron transfer process instead of the oxygen transfer. In the case of catalysts **5** and **7** the adduct is not as electron poor as that of **6**; epoxidation can then take place as well as DPPH oxidation. Nevertheless, when the catalytic system is used for preparative purposes, *i.e.* in the presence of a large excess of oxidant with respect to the catalyst, the independence of W_{cSt} on $[AcOOH]_0$ excludes the pathway which involves '**A**' in alkene epoxidation.

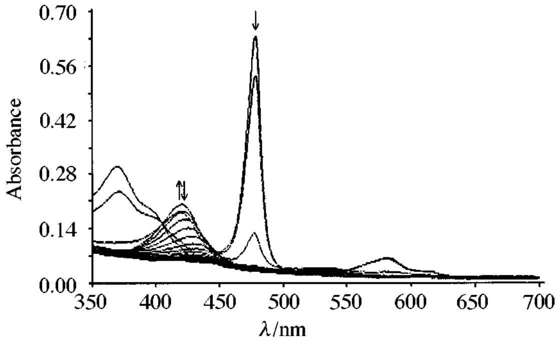

Fig. 5 Visible spectra changes for the reaction of TDCPPMnCl (0.7×10^{-5} M) and AcOOH (3.8×10^{-3} M) at 20 °C in CH_2Cl_2; repetitive interval scan 30 s

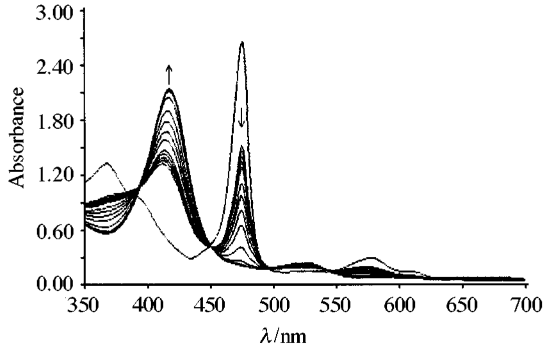

Fig. 6 Visible spectra changes for the reaction of TDCPPMnCl (2×10^{-5} M) and AcOOH (0.01 M) at 20 °C in CH_3CN; repetitive interval scan 30 s

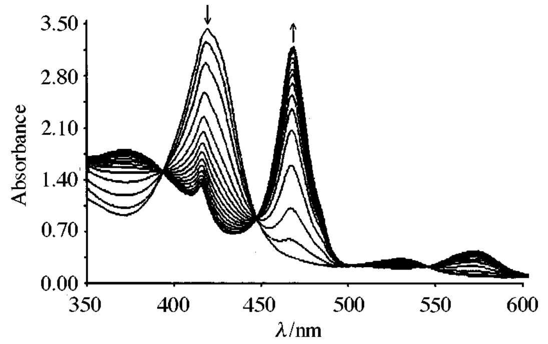

Fig. 7 Visible spectra changes for the reaction of TDCPPMnCl (2×10^{-5} M), AcOOH (0.01 M) and cSt (0.011 M) at 20 °C in CH_3CN; repetitive interval scan 30 s

Catalyst stability in the presence of AcOOH

In previous work we identified the main structural feature which improves the stability of tetraarylporphyrins in the presence of NaOCl or H_2O_2 as oxygen donors. This feature is the presence of bulky and electron-withdrawing substituents on the *ortho* positions of the *meso* phenyl rings.[11]

In an extension of this work on the possibility of carrying out the oxidation of different alkenes and alkanes on a preparative scale, we needed to change the solvent due to the poor solubility of most hydrocarbons in CH_3CN. On the basis of our previous experiences CH_2Cl_2 was chosen but, unexpectedly, we found that catalyst survival in this solvent was much lower. The behaviour of Mn-complexes **5**–**7** (2×10^{-5} M) in CH_2Cl_2 and CH_3CN in the presence of a large excess of AcOOH (10^{-2} M) was followed by visible spectroscopy (between 350–700 nm at 20 °C) under conditions similar to those used for preparative purposes. In CH_2Cl_2, catalysts **6** and **7** generate a short lived species with λ_{max} at 415 nm that rapidly disappears, showing complete macrocycle destruction in *ca.* 1 min; Mn-porphyrin **5** showed a similar behaviour but the unknown species lasted longer (*ca.* 4 min) (Fig. 5). In CH_3CN we could observe a higher stability of the species with absorbance at 415 nm for both **6** and **7** and, surprisingly, the persistence of the same species formed with catalyst **5** (Fig. 6). By the addition of cSt, in equimolar amounts with respect to the peracid, the Mn^{III}-porphyrin was regenerated together with the formation of cStO (Fig. 7). The characterization of this species will be the object of further studies which will be reported elsewhere.

Conclusions

(*i*) The mechanism of PMnCl (P = TDCPP, NO_2Pc, TAP) interaction with peracetic acid in CH_3CN solutions includes the *reversible* stages of molecular complexe '**A**' 'catalyst · · · oxidant' formation. Transformation of this by an *irreversible* step leads to $PMn^V(O)X$.

(*ii*) The oxidative property of '**A**' in terms of electron transfer capability depends on catalyst structure, while, under the reaction conditions used for the kinetics studies, '**A**' cannot effect alkene epoxidation.

(*iii*) General methods for k_1 and k_2 evaluation are proposed and may be used for determination of rate constant values for any porphyrin-like metallic complexes.

(*iv*) In the absence of substrate, the reaction between Mn-porphyrin **5** and peracetic acid in CH_3CN generates a surprisingly stable species which has not yet been characterized but which seems to feature oxidative properties.

(*v*) These results and the high turnover number obtained in our previous work[1] suggest that the system Mn-porphyrinoid–peracetic acid in CH_3CN proves to be particularly suitable to achieve high yields in alkene epoxidations under simple and mild conditions. In particular the use of a non-sterically protected catalyst, such as phthalocyanine **6**, can be exploited for the epoxidation of *trans*-alkenes which cannot be epoxidized by tetraarylporphyrins.

Acknowledgements

The authors wish to thank the group of Professor E. A. Luk′yanets of the Organic Intermediates and Dyes Institute of Moscow for the generous gift of catalysts **6** and **7**, and Professor P. Beltrame of the Department of Organic and Industrial Chemistry of Milano University for helpful discussions.

This work was supported by the Progetto Strategico Tecnologie Chimiche Innovative, CNR, Roma.

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Paper 6/08205J
Received 20*th November* 1996
Accepted 14*th March* 1997