Oxygen Transfer from Ph_4PHSO_5 to Manganese Porphyrins: Kinetics and Mechanism of the Formation of the Oxo Species in Homogeneous Solution

Sandro Campestrini, Fulvio Di Furia,* Gilles Labat and Fabiola Novello
Centro CNR di Studio sui Meccanismi di Reazioni Organiche, Dipartimento di Chimica Organica, Universita' di Padova, Via Marzolo 1, 35131 Padova, Italia

The kinetics and mechanism of the oxygenation of Mn(TMP)Cl, Mn(TDCPP)Cl and Mn(Br_8TMP)Cl by Ph_4PhSO_5 has been investigated in 1,2-dichloroethane and acetonitrile. In both solvents the reaction takes place only in the presence of species acting as axial ligands of the manganese porphyrins, *e.g.* imidazole or 4-*tert*-butylpyridine whose association constants to the metal have been measured. The rates of disappearance of the manganese porphyrin and of the appearance of the oxo-species, obtained by the stopped-flow technique, are identical within the experimental error. This finding, together with the determination of the kinetic law of the reaction allows us to suggest that the oxygen transfer process may be a simple bimolecular reaction or that, if an intermediate is formed, it is rather short lived.

Metalloporphyrins catalyse the oxygenation of organic substrates by various oxygen donors.[1] The catalysis involves reactions (1) and (2),[1,2] where M = Fe, Mn, Ru, *etc.*; X = Cl^-,

$$MPX \xrightarrow{\text{Oxygen donor}} OMPX \qquad (1)$$

$$OMPX + Sub \longrightarrow MPX + SubO \qquad (2)$$

ClO_4^-, AcO^-, *etc.*; P = Porphyrin ring; and oxygen donor = PhIO, RCO_3H, NaOCl, $KHSO_5$, H_2O_2, RO_2H, *etc.* A formal analogy can be drawn with the oxidation by peroxides catalysed by transition metal (*e.g.* Ti, V, Mo, W) complexes.[3] In both systems the interaction of an oxygen donor with a metallic centre forms an intermediate which is a stronger oxidant than the parent oxygen donor.[3c] In metal-catalysed oxidations the isolation and characterization of the active intermediates, which are peroxometal complexes, greatly facilitated the understanding of the mechanism.[3-5] By contrast, the intermediates' metalloporphyrinato-oxo species seldom can be isolated.[1n] This is probably one of the reasons why some important mechanistic aspects of the oxygenation of organic substrates catalysed by metalloporphyrins are still a matter of debate. As an example, the occurrence of an intermediate has been postulated, but never detected, in olefins' epoxidation.[6] Moreover, different proposals have been put forward concerning the nature of such an intermediate[7] and on the rate limiting step.[8] Furthermore, the mechanistic studies are generally carried out under phase-transfer conditions in which the processes of transfer of the various species from one solvent to the other and the effect of the phase transfer agents increase the complexity of the system.[9] Therefore we have collected our spectroscopic, conductometric and kinetic data in a homogeneous system, *i.e.* in 1,2-dichloroethane or in CH_3CN solution. In the present study we focus our attention on reaction (1), *e.g.* on the oxygenation of three different manganese porphyrins, *i.e.* 5,10,15,20-tetrakis(2′,4′,6′-trimethylphenyl)porphyrinate[Mn(TMP)Cl], 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrinate [Mn(TDCPP)Cl] and 5,10,15,20-tetrakis(2′,4′,6′-trimethylphenyl)-β-octabromoporphyrinate [Mn(Br_8TMP)Cl] with tetraphenylphosphonium monopersulfate, Ph_4PHSO_5.

Results and Discussion

Ph_4PHSO_5, whose preparation is described in the Experimental section, is particularly suitable for mechanistic studies of catalysis by metalloporphyrins. It can be obtained consistently with a high degree of purity (> 97%) and it is fairly soluble, up to *ca.* 0.1 mol dm^{-3}, in 1,2-dichloroethane at 25 °C. As an additional advantage, Ph_4PHSO_5 under our experimental conditions, in the absence of manganese porphyrins, does not epoxidize olefins such as styrene or cyclooctene, so that in kinetic studies of olefins' epoxidation the contribution of the uncatalysed process can be neglected. Attempts to employ the analogous Bu_4NHSO_5 were frustrating. In our hands, subsequent preparations carried out under identical conditions provide materials of different purity which, at any rate, was not greater than 85%, the other salts present being Bu_4NHSO_4 and $(Bu_4N)_2SO_4$. The former inhibits the epoxidation of olefins by Bu_4NHSO_5 in the presence of the metalloporphyrins through a mechanism which is, as yet, unknown.

Initially, we observed that Ph_4PHSO_5 alone does not transfer its oxygen to the three manganese porphyrins examined in this work. This was unequivocally established by a spectroscopic investigation. Thus, even by adding a 1000-fold excess of Ph_4PHSO_5 to a 6.0×10^{-6} mol dm^{-3} solution of Mn(TMP)Cl, Mn(TDCPP)Cl and Mn(Br_8TMP)Cl in 1,2-dichloroethane, at 15 °C, no spectral changes were observed in the region of the Soret band of the three manganese metalloporphyrins—which occurs at 476, 478 and 503 nm respectively. By contrast, when the same experiment was carried out using *m*-chloroperbenzoic acid (MCPBA) instead of Ph_4PHSO_5, the spectroscopic analysis of the reaction mixture revealed the almost immediate disappearance of the Soret band of the manganese porphyrins and the appearance of a new band at lower wavelength. As an example, in the case of Mn(TMP)Cl, the new band is found at 403 nm. In order to form the same species from Ph_4PHSO_5 in 1,2-dichloroethane it was necessary to add to the reaction mixture either imidazole or a pyridine derivative, *i.e.* species which, acting as axial ligands of the metalloporphyrins, are known to accelerate also the catalytic oxidations of organic substrates.[1f,p] The disappearance of the Soret band of Mn(Br_8TMP)Cl upon addition of Ph_4PHSO_5 and the appearance of the new band at 457 nm in the presence of pyridine is shown in Fig. 1. The attribution of the band at 457 nm to the oxo-species was based on the following experiment. Immediately after the formation of the new band, an excess of cyclooctene was added. This caused in a few seconds the disappearance of the band at 457 nm whereas the band at 503 nm was completely restored. The GC analysis of the reaction

Table 1 Association constants of imidazole and 4-*tert*-butylpyridine to metalloporphyrins (MP) as determined by the Walker procedure (see text)[a]

Solvent	MP	Ligand	$K_1/10^2$ $\mathrm{dm^3\,mol^{-1}}$	$\beta_2/10^5$ $\mathrm{dm^6\,mol^{-2}}$	$K_2/10^2$ $\mathrm{dm^3\,mol^{-1}}$
$ClCH_2CH_2Cl$	Mn(TMP)Cl	Imidazole	5.8 ± 0.6	3.9 ± 0.3	6.9 ± 1.1
$ClCH_2CH_2Cl$	Mn(TMP)Cl	4-*tert*-Butylpyridine	1.8 ± 0.8	0.3 ± 0.05	1.7 ± 1.0
$ClCH_2CH_2Cl$	Mn(TDCPP)Cl	Imidazole	—	37 ± 2	—
$ClCH_2CH_2Cl$	Mn(TDCPP)Cl	4-*tert*-Butylpyridine	—	0.6 ± 0.03	—
CH_3CN	Mn(TMP)Cl	Imidazole	43 ± 5	—	—
CH_3CN	Mn(TMP)Cl[b]	Imidazole	26 ± 4	3.2 ± 1	1.2 ± 0.5
CH_3CN	Mn(TMP)Cl[b]	4-*tert*-butylpyridine	8.0 ± 1.3	1.3 ± 1	1.6 ± 1.4

[a] $[\mathrm{MP}] = 6.5 \times 10^{-6}\ \mathrm{mol\,dm^{-3}}$, $T = 30$ °C. [b] $[\mathrm{MP}] = 1.6 \times 10^{-5}\ \mathrm{mol\,dm^{-3}}$.

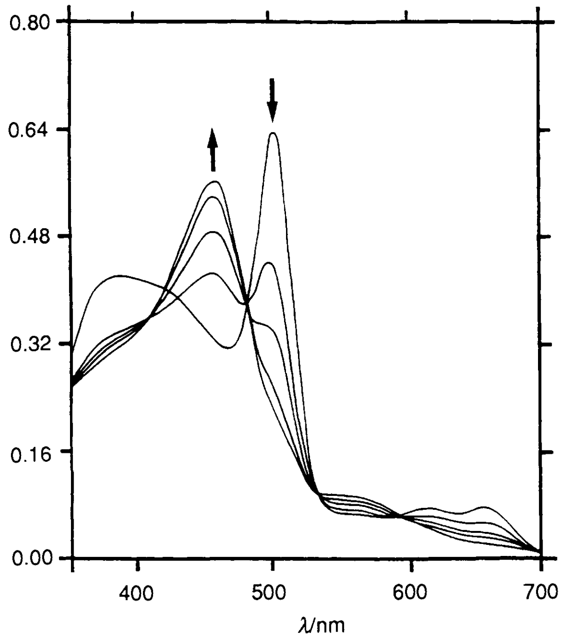

Fig. 1 Spectral changes observed during the reaction of Mn(Br_8TMP)Cl (1.6×10^{-5} mol dm^{-3}) with Ph_4PHSO_5 (3.0×10^{-2} mol dm^{-3}) in the presence of pyridine (1.5×10^{-3} mol dm^{-3}), in 1,2-dichloroethane at 25 °C; the time interval between each spectrum is 40 s

mixture revealed that a quantitative yield of cyclooctene oxide, based on the amount of Ph_4PHSO_5 added, was obtained. Control experiments confirmed that in the absence of the manganese porphyrins, the oxidation of cyclooctene does not occur.

Given the crucial role played by the axial ligand we have studied the association equilibria of imidazole and 4-*tert*-butylpyridine to the three manganese porphyrins in the absence of the oxidant by a classical spectroscopic method. Details on the procedure, firstly proposed by Walker,[10] are reported in the Experimental section. The measurements were carried out in 1,2-dichloroethane and, for comparison purposes, also in CH_3CN, aiming at establishing the relevance of the polarity of the solvent in affecting the association equilibria. Note that in classical biphasic systems, owing to the presence of the aqueous phase and of the phase-transfer agents the polarity of the organic phase is probably greater than that of the pure solvents. Table 1 collects the values of the association constants thus determined.

The Walker method, as well as other spectroscopic procedures, suffers from intrinsic limitations if only small spectral changes must be used. In the present study it was not possible to measure all the association constants. In fact, in some instances, the plots of the absorbance of the Soret band as a function of the concentration of the ligand added, instead of straight lines,[10] were curved. However, in other experiments two straight lines were observed. This indicates that there are two equilibrium processes, leading to the formation of a monocoordinated and a biscoordinated manganese porphyrin respectively, as shown in Scheme 1. In Scheme 1 the presence of the chloride anion has been omitted for the sake of simplicity.

$$\mathrm{MP} + \mathrm{L} \overset{K_1}{\rightleftharpoons} \mathrm{MPL} \qquad (3)$$

$$\beta = K_1K_2$$

$$\mathrm{MPL} + \mathrm{L} \overset{K_2}{\rightleftharpoons} \mathrm{MPL_2} \qquad (4)$$

L = Pyridine, imidazole, *etc.*

Scheme 1

It is observed that K_1 and K_2 values are similar in 1,2-dichloroethane whereas, in CH_3CN, K_1 is considerably larger than K_2. To establish the role of the chlorine atom, which may be either covalently bound to the metal or present as the chloride anion of an ion pair in which the manganese porphyrin is the cation, we have carried out a series of conductometric measurements whose results are shown in Figs. 2 and 3.

In 1,2-dichloroethane, the conductivity of Mn(TMP)Cl, in the absence of added ligand 4-*tert*-butylpyridine, is almost zero. The same is observed in the range of occurrence of MPL (Scheme 1). When the excess of L over MP is large enough to allow the formation of MPL_2 the conductivity sharply increases reaching then a plateau at larger concentrations of the ligand. Such conductivity values are measured by subtracting from the total conductivity that of the ligand obtained by separate experiments. In CH_3CN, a conductivity is already measured for MP alone. Upon addition of L the conductivity continuously increases reaching eventually a plateau when all the manganese porphyrin is in the form of MPL_2. Thus it is likely that in 1,2-dichloroethane both MP and MPL are covalent compounds still containing the chloride atom and that MPL_2 has an ion-pair character, whereas in CH_3CN, all the species, *i.e.* MP, MPL and MPL_2 occur, at least in part, as ion pairs. Thus, the conductivity is due to the partial dissociation of such ion pairs. The mechanistic consequences of these observations will be discussed in the appropriate section.

A kinetic study of the oxygen transfer reactions from Ph_4PHSO_5 to the manganese porphyrins in 1,2-dichloroethane was undertaken. In principle, the oxo species may be formed by both processes of eqns. (5) and (6).

$$\mathrm{MPL} + \text{Oxygen donor} \xrightarrow{k_1} \mathrm{MPLO} \qquad (5)$$

$$\mathrm{MPL_2} + \text{Oxygen donor} \xrightarrow{k_1'} \mathrm{MPLO} + \mathrm{L} \qquad (6)$$

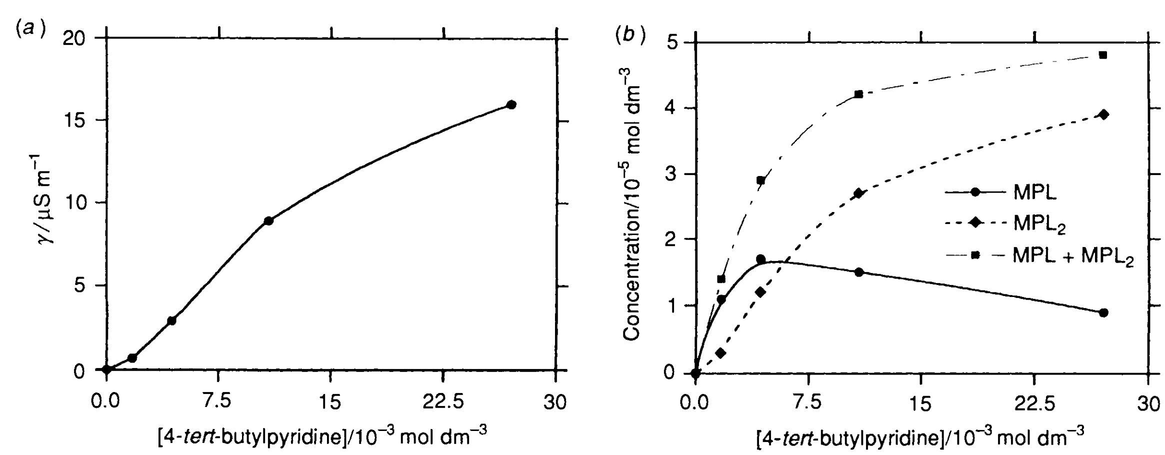

Fig. 2 (*a*) Conductivity of Mn (TMP)Cl (5.2×10^{-5} mol dm^{-3}), in 1,2-dichloroethane at 25 °C, as a function of 4-*tert*-butylpyridine concentration; (*b*) distribution of MPL, MPL_2 and MPL + MPL_2 calculated on the basis of K_1 and K_2 values provided by Walker's spectroscopic method

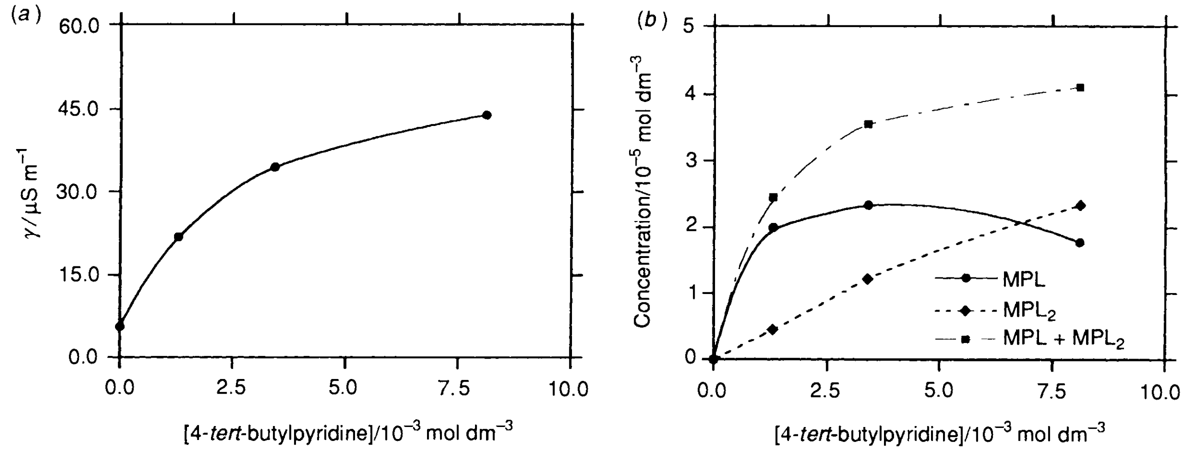

Fig. 3 (*a*) Conductivity of Mn(TMP)Cl (4.4×10^{-5} mol dm^{-3}), in CH_3CN at 25 °C, as a function of 4-*tert*-butylpyridine concentration; (*b*) distribution of MPL, MPL_2 and MPL + MPL_2 calculated on the basis of K_1 and K_2 values obtained by Walker's spectroscopic method

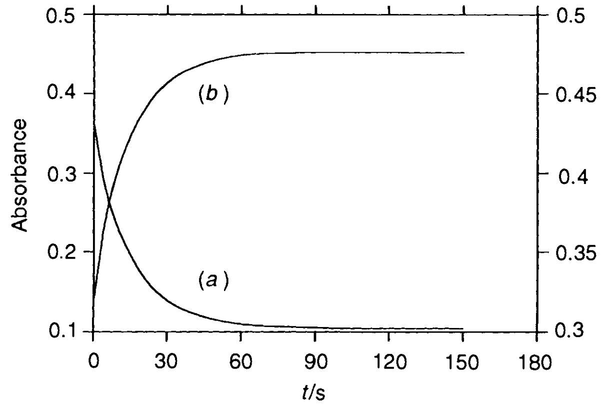

Fig. 4 Plot of A at 473 (*a*) and 403 nm (*b*) *vs.* t for the reaction of Mn(TMP)Cl (6.5×10^{-6} mol dm^{-3}) with Ph_4PHSO_5 (1.35×10^{-2} mol dm^{-3}) in the presence of imidazole (2.6×10^{-3} mol dm^{-3}), in CH_3CN, at 15 °C

The kinetic order of the porphyrin and of the oxidant was determined at a fixed concentration of imidazole by using pseudo-first-order conditions *i.e.* a 100–4000-fold excess of the oxidant over the metalloporphyrin. Subsequently, at a fixed concentration of Mn(TMP)Cl and Ph_4PHSO_5, the effect of increasing imidazole concentration on the rates of formation of MPLO was investigated. The kinetic analysis was facilitated by the observation that, under the appropriate experimental conditions, *i.e.* an excess of the oxidant over the catalyst, MPLO is quantitatively formed, as revealed by the complete disappearance of the Soret band of the manganese porphyrin. Moreover, the lifetime of the oxo species, as shown in Fig. 4, is long enough to assume that concomitant processes of decomposition of MPLO occurring during its fast formation can be neglected.

The observation reported above that the addition of an excess of cyclooctene, once MPLO is formed, completely (>95%) restores the Soret band of the manganese porphyrins not only confirms the quantitative formation of the oxo species but also allows the determination of the molar extinction coefficients, ε, of MPLO which are calculated simply by measuring the absorbance of the oxo species and by dividing such a value by the initial concentration of the manganese porphyrin. The ε values thus obtained are: 85 000 ($ClCH_2CH_2Cl$) and 90 000 (CH_3CN) dm^3 mol^{-1} cm^{-1} for Mn(TMP)Cl, 60 000 ($ClCH_2CH_2Cl$) and 75 000 (CH_3CN) dm^3 mol^{-1} cm^{-1} for Mn(O)(TMP)Cl. The similarity of the ε values of MPL and MPLO is an additional advantage since the same concentrations can be used in the experiments in which the rate of disappearance of the manganese porphyrin and the rate of appearance of the oxo species are measured. The reactions are rather fast, thus requiring the use of the stopped-flow technique. Table 2 collects the pseudo-first-order rate constants measured from the disappearance of the band in the range 478–472 nm and from the appearance of the band at 403 nm respectively.

The agreement between these couples of values is rather satisfactory. This observation may be taken as an indication that an intermediate is not formed in substantial concentration. The kinetic order of Mn(TMP)Cl is one, whereas that of

Table 2 Rate constants for Mn(TMP)Cl oxidation by Ph_4PHSO_5 in the presence of imidazole, in 1,2-dichloroethane, at 15 °C

[Mn(TMP)Cl]/ 10^6 mol dm^{-3}	[Ph_4PHSO_5]/ 10^2 mol dm^{-3}	[Imidazole]/ 10^3 mol dm^{-3}	$k_{obs}(Mn^{III})^a$/ 10^2 s^{-1}	$k_{obs}(Mn^0)^a$/ 10^2 s^{-1}
3.5	1.35	0	*b*	*b*
3.5	1.35	1.30	24	24
6.4	1.35	1.30	22	23
10.6	1.35	1.30	24	25
17.7	1.35	1.30	25	26
28.4	1.35	1.30	24	30
6.5	0.06	1.30	2	3
6.5	0.13	1.30	6	6
6.5	0.33	1.30	11	13
6.5	0.66	1.30	18	18
6.5	1.35	0.69	20	20
6.5	1.35	1.40	30	31
6.5	1.35	3.44	53	51
6.5	1.35	6.17	56	52

[a] Duplicate runs agreed within ±6% which can be considered the error of the rate constants reported. [b] No spectral changes were observed (see text) in a period of several minutes.

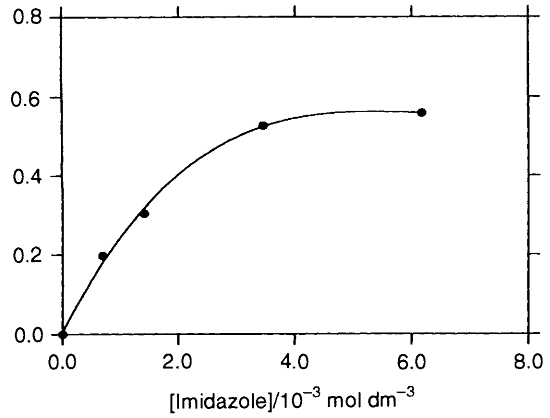

Fig. 5 Dependence of the rate constants on imidazole concentration for the oxidation of Mn(TMP)Cl (6.5 × 10^{-6} mol dm^{-3}) with Ph_4PHSO_5 (1.35 × 10^{-2} mol dm^{-3}), in 1,2-dichloroethane at 15 °C

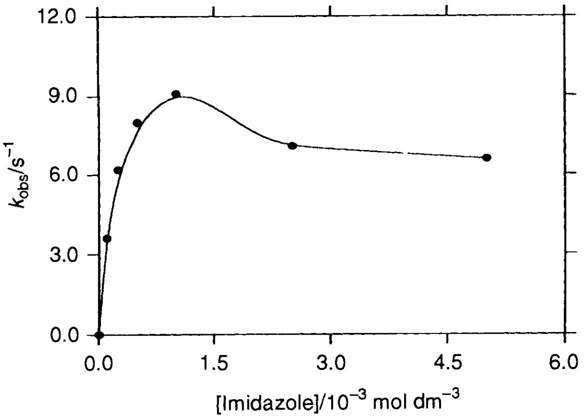

Fig. 6 Dependence of the rate constants on imidazole concentration for the oxidation of Mn(TMP)Cl (6.5 × 10^{-6} mol dm^{-3}) with Ph_4PHSO_5 (1.35 × 10^{-2} mol dm^{-3}), in CH_3CN at 15 °C

Ph_4PHSO_5 tends to become less that one when the concentration of the peroxide increases. Although this might suggest the occurrence of a catalyst–oxidant intermediate, we are keen to attribute such behaviour to aggregation processes involving the peroxide.* On the other hand, if saturation kinetics were operating, a considerable amount of the catalyst would be sequestered to form the intermediate. Accordingly, the close correspondence between the rates of disappearance of Mn^{III} and the appearance of MnO, would be a rather unlikely coincidence. The effect of increasing imidazole concentration in 1,2-dichloroethane, keeping the Mn(TMP)Cl and Ph_4PHSO_5 concentrations constant, is shown in Fig. 5.

Taking into account the fact that by increasing the ligand concentration MPL is converted into MPL_2, the behaviour exhibited in Fig. 5 can be interpreted only by assuming that the rates of formation of MPLO from MPL and from MPL_2 are very similar. The same experiments carried out in CH_3CN provide different results as shown in Fig. 6.

In CH_3CN, the rate of formation of MPLO from MPL is larger than that from MPL_2 thus originating the bell-shaped profile shown in Fig. 6. Note that, also in CH_3CN, MPLO may be formed either from MPL or from MPL_2. The observation that in the absence of ligand the oxo-species is not formed in CH_3CN either, appears to rule out a significant coordination of the solvent to the metal. Alternatively, the unlikely possibility must be considered that CH_3CN is not behaving as the other nitrogen ligands in facilitating the formation of the oxo-species.

On the basis of the results presented, the mechanism of formation of the oxo species from Ph_4PHSO_5 and manganese porphyrins in 1,2-dichloroethane may be described in a more detailed way by the series of reactions of Scheme 2, in which the presence of the chloride atom is now considered.

$$\text{MP–CL} + \text{L} \overset{K_1}{\rightleftharpoons} \text{L–MP–Cl} \qquad (7)$$

$$\text{L–MP–Cl} + \text{L} \overset{K_2}{\rightleftharpoons} (\text{MPL}_2)^+\text{Cl}^- \qquad (8)$$

$$\text{L–MP–Cl} + (\text{Ph}_4\text{P})\text{HSO}_5 \xrightarrow{k_2} (\text{MOPL})^+\text{Cl}^- + \text{Ph}_4\text{PHSO}_4 \qquad (9)$$

$$(\text{MPL}_2)^+\text{Cl}^- + (\text{Ph}_4\text{P})\text{HSO}_5 \xrightarrow{k_2'} (\text{MOPL})^+\text{Cl}^- + \text{Ph}_4\text{PHSO}_4 + \text{L} \qquad (10)$$

Scheme 2

The manganese porphyrins in 1,2-dichloroethane are species in which a covalent bond between the chlorine atom and the metal exists. The association of the first molecule of the ligand takes place at the free axial position as indicated by eqn. (7) leading to a species which is still covalent. The consequence of

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* At larger Ph_4PHSO_5 concentration, *i.e.* >0.02 mol dm^{-3}, control experiments show a decrease of the conductivity of the oxidant in 1,2-dichloroethane that could be due to the formation of ion pairs.

Table 3 Calculated and experimental association and rate constants for the oxidation of Mn(TMP)Cl in the presence of imidazole

	$K_1/10^2$ dm^3 mol^{-1}		$\beta_2/10^5$ dm^6 mol^{-2}		$K_2/10^2$ dm^3 mol^{-1}		k_2/dm^3 mol^{-1} s^{-1}	k_2'/dm^{3}mol^{-1}s^{-1}
Solvent	Calc.	Exp.[a]	Calc.	Exp.[a]	Calc.	Exp.[a]	Calc.	Calc.
$ClCH_2CH_2Cl$	5.5 ± 1.7	5.8 ± 0.6	4 ± 2	3.9 ± 0.3	6.6	6.9	32 ± 6	47 ± 3
CH_3CN	29 ± 12	43 ± 5	30 ± 20	—	10	—	12 ± 3	3.6 ± 0.8

[a] See Table 1.

such an association is the weakening of the metal–chlorine bond so that Cl^- can be displaced by the neutral ligand to form the bis-coordinated adduct. This should be an ion pair as indicated by the conductometric experiments. The effect of the axial ligand in mobilizing the chloride ion is rather strong, since it is observed that the first association constant, K_1 which measures the coordination of the ligand to a vacant site, is very similar to the second constant K_2 which refers to the displacement of Cl^-. Such an effect is largely precedented in metallo-porphyrins' chemistry[11] and it has also been supported by theoretical calculations, though carried out in a related system, which show that the axial ligand in the oxo-species forces the metal ion toward the plane of the porphyrin ring thus increasing the metal–oxygen bond length.[12] The comparison of the behaviour in 1,2-dichloroethane with that observed in CH_3CN provides further evidence supporting the relevant role played by the presence of the first axial ligand. In fact, in the polar solvent CH_3CN, an appreciable amount of the manganese porphyrin is already present as an ion-pair. Thus, the effect of the ligand in facilitating the metal–chlorine bond cleavage is not as crucial as in 1,2-dichloroethane since the cleavage has already taken place to some extent. One might wonder why K_2 in CH_3CN should be smaller than K_1, since K_2 refers to the attack of the ligand on an ion-pair in which the coordination position is completely free, whereas K_1 includes the association constant of both the ion-pair and the covalent species. It is conceivable that the large stabilization operated by the polar solvent on the ion-pair MPL^+Cl^- and also the occurrence of some shielding effect of Cl^- play a role. We may return now to Scheme 2 looking for some independent evidence supporting its validity. For the sake of simplicity the presence of the chlorine atom in the various species is again omitted. The calculated rate law is given by eqn. (11). Taking into account the various equilibria and the

$$R = k_2[\mathrm{MPL}][\text{Oxygen donor}] + k_2'[\mathrm{MPL_2}][\text{Oxygen donor}] \quad (11)$$

appropriate mass balances, eqn. (11) becomes eqn. (12). An immediate check of the validity of eqn. (12) can be obtained by

$$R = [\text{Oxygen donor}]_o \times \left\{k_2 \frac{K_1[\mathrm{L}]_o[\mathrm{MP}]_o}{1 + K_1[\mathrm{L}]_o + \beta_2[\mathrm{L}]_o^2} + k_2' \frac{\beta_2[\mathrm{L}]_o^2[\mathrm{MP}]_o}{1 + K_1[\mathrm{L}]_o + \beta_2[\mathrm{L}]_o^2}\right\} \quad (12)$$

calculating, by means of a mathematical method, K_1, K_2, k_2 and k_2' and by comparing the K_1 and K_2 values thus obtained with those experimentally provided by the Walker spectroscopic procedure. As reported in Table 3, a good agreement between the calculated and the experimental values is observed. This is rather fortunate since the number of data employed is small, owing to experimental difficulties, namely the oxidation of the ligand—the relevance of which increases upon increasing its concentration. At any rate, the experimental curve describing the variation of the rates as a function of the ligand concentration is fairly well defined.

The same conclusion can be made for the data referring to CH_3CN. In passing, it may be noted that the possibility of obtaining K_1 and K_2 by the kinetic procedure described here represents an alternative to the Walker method. A brief comment on the rate constants' values of Table 3 is in order. Therefore, it may be observed that, as previously pointed out, k_2 and k_2' values in 1,2-dichloroethane are similar. Note that k_2 refers to the displacement of the chloride anion, whereas k_2' is the rate constant of the displacement of the neutral ligand, carried out in both cases by the peroxo oxygen of Ph_4PHSO_5. On the basis of the leaving group ability alone, one would expect $k_2' \gg k_2$ even if one takes into account that the chlorine atom in MPLCl is labilized. The mechanism of the substitution reaction is not known but it may be anticipated that a simple S_N2-like attack is too simplistic a picture. It is likely that in determining the energy of the transition state of ligand substitution several factors play a role including the geometry of the transition state itself and the nature of the ligands coordinated to the metal. This aspect, which is a very important one, deserves a more detailed investigation, which is, however, outside the scope of the present work. As far as the results in CH_3CN are concerned, the behaviour observed, *i.e.* $k_2 > k_2'$ is in agreement with the fact that k_2 refers to the attack at a free coordination site of the metalloporphyrins, whereas k_2' is the rate constant for the displacement of the ligand. Of course, in CH_3CN the peculiar requirements of the transition state may play a role also.

We may now summarize some of the relevant information provided by the data presented in this paper. Thus, it has been confirmed that under the conditions adopted, the presence of species capable of acting as axial ligands of the manganese porphyrins is a necessary requisite. In fact, in their absence, the oxo-species is not formed and, of course, no oxidation of organic substrates, *e.g.* olefin epoxidation, occurs. Whereas previous reports suggested that the manganese porphyrin species carrying two coordinated ligands is much less effective in forming the oxo-species,[8c,d,9b,d] under our experimental conditions the reactivity toward Ph_4PHSO_5 of the mono and the bis-coordinated species is similar. Finally, spectroscopic and kinetic evidence has been obtained indicating that the oxygen transfer process does not involve the build-up of an intermediate so that a simple bimolecular reaction may be envisaged.

Experimental

Materials.—1,2-Dichloroethane was purified by distillation over P_2O_5. All the other solvents for the porphyrins' preparation were used as received. Pyridine, 4-*tert*-butylpyridine, imidazole and potassium monopersulfate (Oxone), more than 99% pure, were purchased from Aldrich Chemical Co. and used without further purification. Tetraphenylphosphonium chloride with a purity better than 97% was purchased from Fluka.

5,10,15,20-Tetrakis(2′,4′,6′-trimethylphenyl)porphyrin ($TMPH_2$) and 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrin ($TDCPPH_2$) were synthesized following a slightly modified Lindsay Smith method.[13] 5,10,15,20-Tetrakis(2′,4′,6′-

trimethylphenyl)-β-octabromoporphyrin (Br_8TMPH_2) was obtained by NBS (*N*-bromosuccinimide) bromination of the pyrrole β-positions of $TMPH_2$.[13b,14] The metallation of the porphyrins was performed by conventional methods.[15] Ph_4PHSO_5 was prepared as follows: to a solution of Oxone ($2KHSO_5$ $KHSO_4K_2SO_4$, 4 g in 40 cm^3 deionized water) a solution of tetraphenylphosphonium chloride (2.0 g in 40 cm^3 dichloromethane) was added under vigorous stirring for 3 min. The organic phase was then separated and the crude product recovered after evaporation of the solvent. The crude product was purified by washing with cold water (15 cm^3) and then through repeated crystallizations (three-fold) with a mixture of dichloromethane–pentane. Ph_4PHSO_5 (1.3 g) (54% yield) was thus obtained with a purity better than 97% (iodometric titration). **CAUTION**: this peroxide should be considered as potentially explosive and despite a number of safe syntheses, we never surpassed this preparation scale.

Instruments.—UV–VIS spectra were recorded on a Perkin-Elmer lambda 5 spectrophotometer equipped with thermostatted cells. Kinetic measurements were carried out on an Applied Photophysics Ltd. SF 17 MW stopped-flow instrument. Conductivity experiments were carried out on a Metrohm 660 conductometer.

Kinetic Measurements.—In a typical run, a 2.5×10^{-2} mol dm^{-3} solution of monopersulfate in $ClCH_2CH_2Cl$ or CH_3CN and a 1.25×10^{-5} mol dm^{-3} solution of metalloporphyrin in $ClCH_2CH_2Cl$ or CH_3CN and 1.0×10^{-2} mol dm^{-3} of axial ligand were stored in the two compartments of the stopped-flow instrument and thermostatted at the desired temperature. The reactions, initiated by injecting equal volumes of the two solutions into the mixing cell, were monitored by recording the absorption at the two wavelengths corresponding to the Soret-band of the starting material and of the product. Duplicate runs agreed within ±6% which can be considered the error of the rate constants reported.

Spectroscopic Measurements.—The K_1 and β_2 values were determined as reported by Walker *et al.*,[10] by measuring the absorbance changes of solutions containing the same amount of metalloporphyrin and different axial ligand excesses, at the appropriate wavelength. The K_1 and β_2 values were provided as intercepts of plots of $\log(A - A_0)/(A - A_\infty)$ *versus* axial ligand concentration, which are straight lines with slopes 1 and 2 respectively.

The calculated K_1 and β_2 values, together with the k_2 and k_2' rate constants were obtained from eqn. (12) by a non-linear regression data analysis program (Enz Fitter program).

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