

# Mechanistic studies on the reaction of monopersulfate with a manganese(III) porphyrin in the presence of phenates and benzoates as axial ligands and subsequent epoxidation of olefins in homogeneous solution

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## Abstract

The oxygen transfer reaction from  $\text{Ph}_4\text{PHSO}_5$  to manganese(III) porphyrins in the presence of a series of tetrabutylammonium phenates and benzoates leading to a manganese-oxo species and the subsequent epoxidation of olefin has been studied in dichloroethane. When benzoates act as axial ligands of the catalyst, the Hammett plots obtained by changing the substituents on the phenyl ring of the ligand give negative rho values for both oxene formation and epoxidation. On the contrary, when phenates are employed the Hammett plot for olefin epoxidation provides a positive rho value. This is rationalized by assuming that the variation of the nature of the ligand produces a change of the rate determining step of the catalytic process. In addition, the oxo species formed in the presence of phenates behaves as an electrophilic oxidant whereas that formed in the presence of benzoates has a definite radical character.

*Keywords:* Alkenes; Epoxidation; Oxidation; Manganese; Porphyrins; Peroxomonosulfate

## 1. Introduction

We have previously reported [1,2] that in the oxidizing system which utilizes catalytic amounts of manganese(III)porphyrins and tetraphenylphosphonium monopersulfate ( $\text{Ph}_4\text{PHSO}_5$ ) under homogeneous conditions in dichloroethane (DCE), the presence of a nitrogen base, such as imidazole or pyridine, acting

as axial ligands of the catalyst, is a necessary requisite for the formation of an oxo-manganese species (oxene) [1]. This is the actual oxidant of organic substrates [3]. Also anionic bases such as  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$  and  $\text{CH}_3\text{COO}^-$  allow the formation of oxo-manganese derivatives [4]. Such bases, however, promote the formation of an oxo species which shows spectroscopic and chemical properties different from that formed in the presence of nitrogen bases. In the presence of anionic bases, the oxene exhibits its Soret band at 421 nm and the catalytic oxidation

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of *cis*-stilbene yields a mixture of *cis* and *trans* epoxide together with some benzaldehyde. The oxene formed in the presence of nitrogen bases has its Soret band at 406 nm and the oxidation of *cis*-stilbene leads almost exclusively to the *cis* epoxide [1,2,4].

A potential advantage of anionic bases is that they should resist to oxidation better than the neutral nitrogen ones. A drawback of  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$  and  $\text{CH}_3\text{COO}^-$  is their poor efficiency in promoting the formation of oxene. As an example, the oxygen transfer from  $\text{Ph}_4\text{PHSO}_5$  to  $\text{Mn}(\text{TMP})\text{Cl}$  in the presence of pyridine is at least 100-fold faster than in the presence of the anionic bases, mentioned above, under otherwise identical experimental conditions [1,4]. Therefore, we tried other anionic bases. In this paper we present the results of a kinetic study on the oxygen transfer from  $\text{Ph}_4\text{PHSO}_5$  to manganese 5,10,15,20-tetrakis(2',4',6'-trimethylphenyl)porphyrinate,  $\text{Mn}(\text{TMP})\text{Cl}$ , promoted by phenates and benzoates and on the epoxidation of olefins by the resulting oxo-manganese species. It may be expected that such bases do not lead to significant synthetic improvements compared with neutral nitrogen bases [5]. On the other hand, the results collected provide additional mechanistic information on the general behavior of the oxidizing system.

## 2. Results and discussion

### 2.1. Epoxidation of olefins with $\text{Ph}_4\text{PHSO}_5$ catalyzed by $\text{Mn}(\text{TMP})\text{Cl}$ in the presence of phenates

The oxidation of cyclooctene and *cis*-stilbene with monopersulfate in the presence of catalytic amounts of  $\text{Mn}(\text{TMP})\text{Cl}$  and variously substituted tetrabutylammonium phenates has been studied in DCE at 0°C. Control experiments indicate that the epoxidation does not proceed in the absence of the catalyst and/or of the axial ligand. The oxidation of cyclooctene yields cyclooctene epoxide and that of *cis*-stilbene the

Table 1

Pseudo-first-order constants  $k_1$  ( $\text{s}^{-1}$ ), for the oxidation of 0.12 M cyclooctene or styrene with  $2.0 \times 10^{-2}$  M  $\text{Ph}_4\text{PHSO}_5$  catalyzed by  $5.0 \times 10^{-5}$  M  $\text{Mn}(\text{TMP})\text{Cl}$  in the presence of variously substituted  $1.0 \times 10^{-2}$  M tetrabutylammonium phenates, in DCE, at 0°C

Run	Substrate	X-(C <sub>6</sub> H <sub>4</sub> )-O <sup>-</sup> X =	$k_1 \times 10^5$ , $\text{s}^{-1}$	Yield, %
1	cyclooctene	H	1.9	15
2	cyclooctene	<i>p</i> -CH <sub>3</sub> O	1.3	27
3	cyclooctene	<i>p</i> -Ph	2.1	10
4	cyclooctene	<i>p</i> -Cl	2.3	17
5	cyclooctene	<i>m</i> -Cl	3.2	18
6	cyclooctene	<i>p</i> -NO <sub>2</sub>	5.7	41
7	<i>cis</i> -stilbene	H	2.0	10
8	<i>cis</i> -stilbene	<i>p</i> -NO <sub>2</sub>	10.0	45

corresponding *cis*-epoxide. Therefore, the effect of phenates on the reactivity of the oxene resembles that of neutral nitrogen bases. The reaction rates were measured by determining, at various times, the concentration of the epoxides by GLC analysis. The pseudo first-order rate constants ( $k_1$ ,  $\text{s}^{-1}$ ) were obtained from integrated plots, i.e.  $\ln([\text{epoxide}]_\infty - [\text{epoxide}]_t)$  vs. time which were linear up to 50% reaction. The effect of the substituents of the axial ligand on the rates of epoxidation of the two olefins is illustrated by the data of Table 1 which also collects the yields of the corresponding epoxides.

Such yields are rather low. This is mainly due to the competitive oxidation of the phenate ligand to products whose nature has not been investigated. The observation of strongly colored solutions at the end of the reaction suggests that quinones may be formed [6]. Such a process not only consumes oxidant but also decreases the concentration of available axial ligand. In addition, a self-decomposition of monopersulfate caused by the presence of bases in solution takes place [7]. All these processes have been detected by direct experiments. The occurrence of these processes hampers the study of the first part of the catalytic cycle, i.e. the oxygen transfer from  $\text{Ph}_4\text{PHSO}_5$  to  $\text{Mn}(\text{TMP})\text{Cl}$  forming the oxene. From a kinetic point of view

the experimental rate constants reported in Table 1 refer to at least three parallel processes [8], namely olefin epoxidation, phenate oxidation and oxidant decomposition. In spite of this complication, a satisfactory correlation of such rate constants with the Hammett  $\sigma$  values of the substituents in the phenates ring is found for cyclooctene oxidation (runs 1–6). The positive rho value ( $\rho = 0.63$ ,  $R = 0.98$ ) indicates that electron-withdrawing substituents accelerate the rates. The same effect is operating in *cis*-stilbene oxidation (runs 7 and 8). As a consequence, one may suggest that in the epoxidation step the oxo species is the electrophile and the olefin the nucleophile [9]. Moreover, it may also be suggested that the epoxidation step should be the rate-determining step, rds, of the process. In fact, if the oxo-forming reaction were the rds, electron-withdrawing substituents on the Mn(III)–porphyrin should decrease the rate by decreasing the nucleophilic character of the Mn(III)–porphyrin and a negative rho value should be observed.

More useful information cannot be obtained from such a complicated system. Therefore we decided to study the behavior of benzoates as axial ligands, since they should be less prone to oxidative attack.

## 2.2. Oxidation of Mn(TMP)Cl with Ph<sub>4</sub>PFSO<sub>5</sub> in the presence of benzoates

Before starting, we checked that tetrabutylammonium benzoate PhCOO<sup>−</sup> Bu<sub>4</sub>N<sup>+</sup> is stable under the experimental conditions adopted. In fact, the salt is recovered unchanged after several hours in the presence of the oxidant. A spectroscopic study on the Mn(TMP)Cl oxidation with Ph<sub>4</sub>PFSO<sub>5</sub> in the presence of tetrabutylammonium benzoate shows the disappearance of the Soret band of the manganese(III)porphyrin at 472 nm and the appearance of a second band at 421 nm as already observed for SO<sub>4</sub><sup>2−</sup>, ClO<sub>4</sub><sup>−</sup> and CH<sub>3</sub>COO<sup>−</sup> (see Fig. 1).

The oxo derivative of Mn(TMP)Cl exhibiting the Soret band at 421 nm should be a manganese(IV) oxo species [4]. Alternatively, it could be that the species at 421 nm still contains the monopersulfate molecule. In the light of the results reported below and, in particular, of the reactivity of the species absorbing at 421 nm, the hypothesis of the formation of a Mn(IV)–oxo derivative appears more likely. A kinetic study of the formation of the species absorbing at 421 nm was carried out. The kinetic order of Mn(TMP)Cl and of Ph<sub>4</sub>PFSO<sub>5</sub> was determined

Table 2  
Pseudo-first-order constants  $k_1$  (s<sup>−1</sup>) for Mn(TMP)Cl oxidation by Ph<sub>4</sub>PFSO<sub>5</sub> in the presence of tetrabutylammonium benzoate, in DCE, at 16°C

Run	[Ph <sub>4</sub> PFSO <sub>5</sub> ] × 10 <sup>3</sup> , M	[PhCO <sub>2</sub> N(nBu) <sub>4</sub> ] × 10 <sup>3</sup> , M	[Mn(TMP)Cl] × 10 <sup>6</sup> , M	$k_{\text{obs}, 472 \text{ nm}}$ × 10 <sup>3</sup> , s <sup>−1</sup>	$k_{\text{obs}, 421 \text{ nm}}$ × 10 <sup>3</sup> , s <sup>−1</sup>
1	5.8	5.4	8.1	4.9	5.1
2	8.1	5.4	8.1	7.7	7.8
3	10.0	5.4	8.1	9.5	10.0
4	12.8	5.4	8.1	12.0	13.1
5	8.7	2.3	10.0	10.3	10.6
6	8.7	5.1	10.0	16.8	18.0
7	8.7	10.3	10.0	30.1	32.9
8	8.7	20.7	10.0	61.0	74.0
9	6.0	20.7	6.1	16.4	18.0
10	6.0	20.7	8.1	17.3	18.5
11	6.0	20.7	15.1	13.2	15.9
12	6.0	20.7	20.2	11.9	12.4
13	6.0	20.7	30.3	10.0	10.0

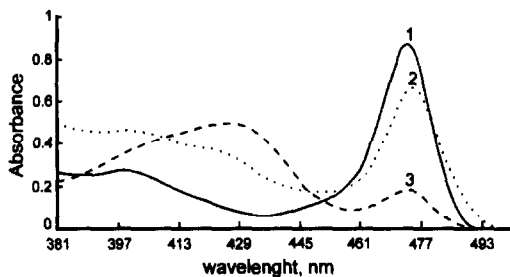


Fig. 1. Spectral changes observed during the reaction of  $1.0 \times 10^{-5}$  M Mn(TMP)Cl with  $1.7 \times 10^{-2}$  M  $\text{Ph}_4\text{PHSO}_5$  in the presence of  $2.0 \times 10^{-2}$  M tetrabutylammonium benzoate, in DCE, at room temperature. (1) Spectrum of Mn(III)TMPCl in the presence of the axial ligand before adding the oxidant. (2) Spectrum recorded 20 s after the addition of the oxidant. (3) Spectrum recorded after 60 s.

at a fixed concentration of benzoate by using pseudo-first-order conditions, i.e. a 200–1600 fold excess of the oxidant over the metalloporphyrin. The kinetic order of benzoate was determined at a fixed concentration of Mn(TMP)Cl and  $\text{Ph}_4\text{PHSO}_5$ . The kinetic data were obtained by following the disappearance of the Mn(TMP)Cl Soret band at 472 nm and, in independent runs, the appearance of the band at 421 nm by using stopped-flow technique. In Table 2 are collected the pertinent results.

The agreement between the  $k_{\text{obs}}$  values obtained is satisfactory, indicating that in the formation of the species absorbing at 421 nm, no intermediates should occur. The kinetic order of the oxidant (runs 1–4), obtained as the slope of a  $\log k_{\text{obs}}$  vs.  $\log[\text{Ph}_4\text{PHSO}_5]$  plot, is 0.99 ( $R = 0.997$ ) by using the data referring to the formation of the species at 421 nm and 0.95 ( $R = 0.998$ ) if the data corresponding to the disappearance of the manganese porphyrin are used. The kinetic order of benzoate (runs 5–8) is 0.91 from both sets of data, with  $R = 0.997$  and  $R = 0.995$  for the product formation and for reagent disappearance respectively. The kinetic order of Mn(TMP)Cl is definitely less than one. Values of 0.62 from product formation ( $R = 0.980$ ) and of 0.68 from reagent disappearance ( $R = 0.995$ ) are found. The kinetic picture is rather different from that of nitrogen bases. In

that case, the order of Mn(TMP)Cl is one whereas that of the axial ligand tends to decrease with increasing its concentration indicating the saturation of the catalyst [1]. The order one of the benzoate ligand found here indicates that its association constant to the metalloporphyrin is small, so that saturation of the metalloporphyrin is not reached. The kinetic order of less than one found for the catalyst may be attributed to the peculiar character of the carboxylate anion which may act as a bidentate ligand sharing its oxygen atoms with two molecules of Mn(TMP)Cl in a sort of sandwich-like complex. According to this hypothesis, the decrease of the order of the catalyst as its concentration increases is due to the formation, at the highest Mn(TMP)Cl concentrations employed, of a binuclear manganese complex in which the two nucleophilic metal centers, sharing the negative charge of the carboxylate anion, are less prone to receive the electrophilic oxygen than the mononuclear species which carries the entire negative charge. Further evidence supporting the importance of the negative charge of the axial ligand in determining the oxidizability of the manganese porphyrin is given by the reactivity pattern observed within the series of substituted benzoates. The results are collected in Table 3.

The rho values found for Mn(TMP)Cl oxidation are  $-0.83$  ( $R = 0.996$ ) and  $-0.85$  ( $R = 0.998$ ) from the data corresponding to the appearance of the product and to the disappear-

Table 3

Pseudo-first-order constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) for the oxidation of  $9.9 \times 10^{-6}$  M Mn(TMP)Cl with  $7.6 \times 10^{-3}$  M  $\text{Ph}_4\text{PHSO}_5$  in the presence of  $2.0 \times 10^{-3}$  M benzoates, in DCE, at  $16^\circ\text{C}$

Run	X-( $\text{C}_6\text{H}_4$ )- $\text{CO}_2^-$ X =	$k_{\text{obs}, 472 \text{ nm}}$ $\times 10^3, \text{s}^{-1}$	$k_{\text{obs}, 421 \text{ nm}}$ $\times 10^3, \text{s}^{-1}$
1	H	11.3	11.7
2	<i>p</i> -MeO	21.5	22.3
3	<i>m</i> -Cl	0.62	0.65
4	<i>m</i> -MeO	10.1	11.2
5	<i>p</i> -NO <sub>2</sub>	0.27	0.29

ance of the reagent, respectively. The negative rho value is in agreement with the commonly accepted mechanism in which the catalyst is the nucleophile and  $\text{Ph}_4\text{PHSO}_5$  is the electrophile [10].

### 2.3. Epoxidation of olefins with $\text{Ph}_4\text{PHSO}_5$ catalyzed by $\text{Mn}(\text{TMP})\text{Cl}$ in the presence of benzoates

Under conditions similar to those employed in the study of oxene formation, the epoxidation of olefins was investigated. Also in this case the yields are rather low. Nevertheless, the system is less complicated than that employing phenates. Here, in fact, as confirmed by direct experiments, together with epoxidation the only other reaction taking place is the base-catalyzed decomposition of the oxidant. *cis*-Stilbene gives a mixture of *cis* and *trans* epoxide, and benzaldehyde in the ratio 2.2:1.4:1.0. This result is in line with the behavior of the oxidative system in the presence of other anionic axial ligands such as  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$  and  $\text{CH}_3\text{COO}^-$  which also promote a non-stereospecific oxidation of *cis*-stilbene [4]. Note that with phenates as ligands the oxidation was highly stereospecific. This finding suggests that two different oxidizing agents are formed in the two systems. In particular, the homolytic character of the oxidation promoted by benzoates suggests that the resulting oxo species has a definite radical character. This agrees with the hypothesis that the species absorbing at 421 nm is a Mn(IV) oxo-derivative. The oxidation of cyclooctene with  $\text{Ph}_4\text{PHSO}_5$  catalyzed by  $\text{Mn}(\text{TMP})\text{Cl}$  in the presence of variously substituted benzoates has also been studied. The observation that the epoxide is the only product suggests that the radical oxidant maintains a certain degree of selectivity. The results are collected in Table 4.

Probably, the most interesting information is provided by the rho value obtained by plotting  $\log(k_x/k_H)$  vs. the Hammett  $\sigma$  values of the substituents in the ring of benzoate ligands. This rho value is  $-0.97$  ( $R = 0.988$ ), i.e. very simi-

Table 4

Pseudo-first-order constants  $k_1$  ( $\text{s}^{-1}$ ), for the oxidation of 0.12 M cyclooctene with  $2.0 \times 10^{-2}$  M  $\text{Ph}_4\text{PHSO}_5$  catalyzed by  $5.0 \times 10^{-5}$  M  $\text{Mn}(\text{TMP})\text{Cl}$  in the presence of variously substituted  $2.6 \times 10^{-2}$  M tetrabutylammonium benzoates, in DCE, at 0°C

Run	X-(C <sub>6</sub> H <sub>4</sub> )-CO <sub>2</sub> <sup>-</sup> X =	$k_1 \times 10^5$ , $\text{s}^{-1}$	Yield, %
1	H	2.0	23
2	<i>p</i> -CH <sub>3</sub> O	4.0	15
3	<i>m</i> -Cl	0.7	20
4	<i>m</i> -CH <sub>3</sub> O	1.5	39
5	<i>p</i> -NO <sub>2</sub>	0.4	24

lar in magnitude and in sign to that found for  $\text{Mn}(\text{TMP})\text{Cl}$  oxidation in the absence of olefin ( $\rho = -0.84$ ,  $R = 0.998$ ). This suggests that the rds for the catalytic oxidation of olefins is, in this case, the formation of the oxo-manganese species. As a consequence the second step, i.e. the oxygen transfer to the carbon-carbon double bond is kinetically inaccessible.

The rho value for olefin epoxidation in the presence of phenates has been measured to be 0.63. As mentioned before, such a positive rho value may be interpreted by assuming that the formation of the oxene is the fast reaction. It seems unlikely that phenates behave differently, at least in terms of the electronic effects, from benzoates. Consequently, it is reasonable to assume, as we have done, that in the case of benzoates the oxygen transfer to the metalloporphyrin is the rds.

The effect of increasing benzoate concentration on the cyclooctene epoxidation rates has also been studied. The results are presented in Table 5, together with the yields of epoxide.

Particularly with the *p*-OCH<sub>3</sub> derivative, a bell-shaped behavior is observed. The rates increase with increasing benzoate concentration up to a maximum and then decrease. We suggest that this behavior is related to the occurrence of a specific interaction between the oxene and the benzoate. The oxo oxygen atom in the oxene is electrophilic. Its interaction with the negative charge of the carboxylate anion reduces this electrophilic character. By increas-

Table 5

Pseudo-first-order constants  $k_1$  ( $s^{-1}$ ), for the oxidation of 0.12 M cyclooctene with  $2.0 \times 10^{-2}$  M  $\text{Ph}_4\text{PHSO}_5$  catalyzed by  $5.0 \times 10^{-5}$  M  $\text{Mn}(\text{TMP})\text{Cl}$  at various concentration of different tetrabutylammonium benzoates, in DCE, at  $0^\circ\text{C}$

Run	X-(C <sub>6</sub> H <sub>4</sub> )-CO <sub>2</sub> <sup>-</sup> X =	[X-(C <sub>6</sub> H <sub>4</sub> )-CO <sub>2</sub> <sup>-</sup> ] × 10 <sup>2</sup> , M	$k_1 \times 10^5$ , $s^{-1}$	Yield, %
1	H	1.0	1.4	3
2	H	2.6	2.0	23
3	H	5.1	2.6	10
4	H	10.2	1.3	11
5	<i>p</i> -CH <sub>3</sub> O	1.0	2.1	29
6	<i>p</i> -CH <sub>3</sub> O	2.6	4.0	38
7	<i>p</i> -CH <sub>3</sub> O	5.2	2.2	15
8	<i>p</i> -CH <sub>3</sub> O	10.3	1.7	12

ing the benzoate concentration, the relevance of such interaction increases and the rates eventually decrease.

We may now summarize the information provided by the data presented in this paper. It has been shown that phenates and benzoates may act as axial ligands of manganese porphyrins thus allowing the formation, in the presence of an oxidant, of an oxidized manganese porphyrin derivative which carries out the oxidation of organic substrates. However, phenates and benzoates behave differently in spite of their common anionic nature; thus, phenates promote the formation of an oxene species akin to what happens in the presence of nitrogen bases, i.e. it is an electrophilic oxidant which stereospecifically epoxidizes *cis*-stilbene. On the contrary, benzoates give an oxo-metalloporphyrin derivative with a radical character. Moreover, when benzoates are the ligands of the manganese complex, the formation of the oxene is the rds of the catalytic process, whereas, in the case of phenates, the slow step is the oxygen transfer to the olefin. The suggestion that the rates of the two steps of the catalytic process may be similar so that changes in the rds, depending on various parameters, may be expected, has been previously made [2]. Finally, the occurrence of specific interactions between the 'oxene' and anionic axial ligands which reduce the efficiency

of the catalytic oxidative process at high benzoate concentrations has been observed.

### 3. Experimental section

#### 3.1. Materials

1,2-Dichloroethane (DCE) was purified by distillation over  $\text{P}_2\text{O}_5$ . Tetramesitylporphyrin (TMPH<sub>2</sub>) was synthesized following a slightly modified Lindsay Smith method [11]. The metallation of TMPH<sub>2</sub> with  $\text{Mn}(\text{II})(\text{OAc})_2$  was performed by conventional methods [12].  $\text{Ph}_4\text{PHSO}_5$  was prepared and purified as previously reported [1]. Tetrabutylammonium salts of benzoates and phenates were prepared by mixing the appropriate benzoic acids or phenols with a stoichiometric amount of tetrabutylammonium hydroxide (1.5 M solution in water). The solvent was then removed by distillation under vacuum. The remaining material was dissolved in dichloromethane and dried over magnesium sulfate. After removal of the drying agent and evaporation of the solvent, the salt was obtained. The purity of the products were checked by <sup>1</sup>H-NMR. Peroxomonosulfate triple salt (oxone), tetraphenylphosphonium chloride, *cis*-stilbene, cyclooctene and 1,2-dibromobenzene (internal GLC standard) were all commercially available, high purity products (Aldrich), and used as received.

#### 3.2. Instruments

UV-Vis spectra were recorded on a Perkin Elmer lambda 5 spectrophotometer equipped with thermostated cells. Kinetic measurements of  $\text{Mn}(\text{TMP})\text{Cl}$  oxidation rates were carried out on an Applied Photophysics Ltd. SF 17 MW stopped-flow instrument. The concentration of epoxides in the oxidation of olefins was determined by GLC analysis (on the basis of a previously calculated response factor toward an appropriate internal standard) on a Carbowax 20 M 10% (1.8 m column) adsorbed on Chro-

mosorb WAW-DMCS 80/100; the GC was a Varian 6000 equipped with a Shimadzu C-R4 A data processor.

### 3.3. Kinetic measurements of Mn(TMP)Cl oxidation

In a typical run, a  $1.5 \times 10^{-2}$  M solution of monopersulfate in DCE and a  $2.0 \times 10^{-5}$  M solution of Mn(TMP)Cl and of  $1.0 \times 10^{-2}$  M of axial ligand in DCE, were stored in the two compartments of the stopped-flow apparatus and thermostated at 16°C. The reactions, initiated by injecting equal volumes of the two solutions into the mixing cell, were monitored by following the decrease of the absorbance at the wavelength corresponding to the maximum absorption of Mn(TMP)Cl Soret band in the presence of the axial ligand (472 nm) and the increase of the absorbance of the products (421 nm). Duplicate runs agreed to within  $\pm 5\%$ , which can be considered the error of the rate constants reported in Tables 2 and 3.

### 3.4. Kinetic measurements of catalytic olefins oxidation

Typically, the reactions were initiated by adding 2 ml of a  $4.0 \times 10^{-2}$  M  $\text{Ph}_4\text{PHSO}_5$  solution in DCE to a 3 ml of a  $1.0 \times 10^{-4}$  M Mn(TMP)Cl, 0.3 M olefin, 0.1 M axial ligand and  $4.0 \times 10^{-2}$  M 1,2-dibromobenzene (internal standard) solution in DCE, under magnetic stirring in a jacketed reactor thermostated at 0°C. Aliquots of the reaction mixture were withdrawn at various appropriate time intervals, quenched with  $\text{Ph}_3\text{P}$  and analyzed by gas chromatography. Duplicate runs agreed to within  $\pm 4\%$ , which can be considered the error of the

rate constants reported in Table 1, Tables 4 and 5.

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## References

- [1] S. Camestrini, F. Di Furia, G. Labat and F. Novello, *J. Chem. Soc., Perkin Trans. 2*, (1994) 2175.
- [2] S. Camestrini, F. Di Furia, P. Ghiotti, F. Novello and C. Travaglini, *J. Mol. Catal.*, in press.
- [3] (a) J.T. Groves, W.J. Kruper and R.C. Haushalter, *J. Am. Chem. Soc.*, 102 (1980) 6375. (b) J.R. Lindsay Smith and P.R. Sleath, *J. Chem. Soc., Perkin Trans. 2*, (1982) 1009. (c) K. Yamaguchi, Y. Watanabe and I. Morishima, *J. Am. Chem. Soc.*, 115 (1993) 4058.
- [4] S. Camestrini, J.O. Edwards, F. Di Furia and F. Novello, *J. Mol. Catal. A*, 97 (1995) 79.
- [5] (a) S. Banfi, F. Montanari, S. Quici, *J. Org. Chem.*, 54 (1989) 1850. (b) F. Montanari, S. Banfi, S. Quici, *Pure Appl. Chem.*, 61 (1989) 1631.
- [6] W.I. Taylor and A.R. Battersby (Eds), *Oxidative Coupling of Phenol*, Marcel Dekker, New York, 1967, Ch. I.
- [7] D.L. Ball and J.O. Edwards, *J. Am. Chem. Soc.*, 78 (1956) 1125.
- [8] J.F. Bunnett, in E.S. Lewis (Ed.), *Investigation of Rates and Mechanism of Reactions, Part I*, 3rd Ed., John Wiley and Sons, New York, 1974, Ch. IV.
- [9] O. Bortolini and B. Meunier, *J. Chem. Soc., Perkin Trans. 2*, (1984) 1967.
- [10] (a) R.D. Arasasingham and T.C. Bruice in D.H.R. Burton (Ed.), *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, Plenum Press, New York, 1993. (b) T.C. Bruice in J.F. Lieberman and A. Greenberg (Eds), *Mechanistic Principles of Enzyme Activity*, VCH, New York, 1988, Ch. 6.
- [11] (a) J.R. Lindsay Smith and R.W. Wagner, *J. Org. Chem.*, 54 (1989) 828. (b) P. Hoffmann, A. Robert and B. Meunier, *Bull. Soc. Chim. Fr.*, 129 (1992) 85.
- [12] (a) A.D. Adler, F.R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, 32 (1970) 2443. (b) A. Robert, M. Momenteau, B. Look and B. Meunier, *Inorg. Chem.*, 30 (1991) 706.