Olefins epoxidation by Ph$_4$PHSO$_5$ catalyzed by manganese porphyrins: A novel mechanistic proposal

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Abstract

The epoxidation of three olefins, cyclooctene, styrene and *cis*-stilbene by Ph$_4$PHSO$_5$, catalyzed by Mn(TMP)Cl, has been studied in dichloroethane at 0°C. In the absence of imidazole the reaction does not proceed. When the axial ligand is present the oxidation provides the corresponding epoxides. *Cis*-stilbene stereospecifically yields *cis*-stilbene oxide. The epoxidation rates linearly depend on Ph$_4$PHSO$_5$ and catalyst concentrations. By increasing the axial ligand concentration the rates increase up to a plateau. This occurs when all the manganese–porphyrin has been complexed by imidazole to form the bis-coordinated adduct. Also by increasing the olefin initial concentration the rates reach a plateau. This behavior, which might be taken as evidence of the formation of a Michaelis–Menten type intermediate, is alternatively rationalized here on the basis of a balance of the rates of the various steps of the overall process. In particular it is envisaged that at high olefin concentration the oxygen transfer to the double bond from the oxo-manganese porphyrin becomes at least as fast as the oxygen transfer from Ph$_4$PHSO$_5$ to the manganese porphyrin.

Keywords: Tetraphenylphosphonium peroxomonosulfate; Manganese; Porphyrins; Olefins; Epoxidation mechanism
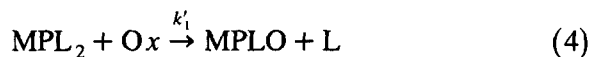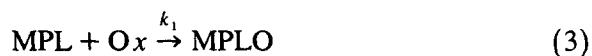
1. Introduction

The epoxidation of olefins by various oxygen donors in the presence of Mn(III)–porphyrinato catalysts has been extensively studied [1–4] from both a synthetic [1] and a mechanistic [2,4] point of view. While the best conditions for fast reactions, high conversions and large turnover numbers have been established [2,3], the mechanism of epoxidation is still a matter of debate [4]. The controversy concerns some basic as-

pects. As an example, it is not yet unambiguously established whether the oxygen transfer from the oxo-manganese porphyrin to the double bond is a bimolecular or a two-step process [5]. The tendency towards a zero-order dependence upon increasing the substrate concentration has been taken as evidence of the occurrence of an intermediate [4]. On the other hand it has been pointed out that such behavior does not necessarily imply saturation of the oxidant, i.e. the occurrence of a Michaelis–Menten-type intermediate [6]. Also on the nature of the putative intermediate several hypotheses have been

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put forward [7]. These include oxo-metallo-cycles [7](a), carbocations [7](b), radicals [7](c), and ion pairs [7](d). A major concern in proposing the structure of the intermediate appears to be the need to rationalize the large stereoselectivity of the epoxidation [8].

Recently we have prepared a novel oxygen donor, i.e. tetraphenylphosphonium monopersulfate, Ph_4PHSO_5, which shows some advantages over other oxidants as far as mechanistic studies are concerned [9,10]. In fact Ph_4PHSO_5 can be obtained with a high degree of purity ($> 97\%$) and it is also soluble in non polar solvents. This allows to carry out kinetic experiments under homogeneous and fairly well controlled conditions [9,10]. We have reported [9] the results of a kinetic study of the oxygen transfer from Ph_4PHSO_5 to manganese porphyrins (MP) in dichloroethane (DCE). Three different manganese porphyrins were examined (Mn(TMP)Cl = 5,10,15,20-tetrakis (2',4',6'-trimethylphenyl)-porphine manganese(III) chloride, Mn(TDCPP)Cl = 5, 10,15,20-tetrakis (2',4'-dichlorophenyl)-porphine manganese(III) chloride, $Mn(Br_8TMP)Cl$ = 5,10,15,20-tetrakis (2',4',6'-trimethylphenyl)-2,3,7,8,12,13,17,18-octabromo-porphine manganese(III) chloride).

$$MP + L \overset{K_1}{\rightleftharpoons} MPL \qquad (1)$$

$$MP + 2L \overset{\beta_2}{\rightleftharpoons} MPL_2 \qquad (2)$$

$$MPL + Ox \overset{k_1}{\rightarrow} MPLO \qquad (3)$$

$$MPL_2 + Ox \overset{k'_1}{\rightarrow} MPLO + L \qquad (4)$$

The salient results of our study may be summarized as follows: (1) in the absence of species L (L = pyridine, tert-butylpyridine, imidazole), acting as axial ligands of the porphyrinato complex, the oxygen transfer does not take place even if large excesses of Ph_4PHSO_5 over MP are used; (2) by increasing the concentration of L, monocoordinated MPL and bis-coordinated MPL_2 porphyrinato complexes are formed (Eqs.

(1) and (2)) whose association constants have been measured ($K_1 = 600$ M^{-1}, $\beta_2 = 4 \times 10^5$ M^{-2} for Mn(TMP)Cl and imidazole in DCE at 15°C); (3) MPL and MPL_2 react with Ph_4PHSO_5 at almost the same rate forming the manganese–oxoporphyrinato complex MPLO (Eqs. (3) and (4), $k_1 = 32$ M^{-1} s^{-1}, $k'_1 = 47$ M^{-1} s^{-1} at 15°C again for Mn(TMP)Cl and imidazole in DCE; (4) the reactions of Eqs. (3) and (4) proceed very likely through a bimolecular mechanism. This is suggested by the rate-law of the process which is second-order, first order in both reagents and also by the observation that the rates of disappearance of MPL and MPL_2 correspond to those of appearance of MPLO; (5) MPLO oxidizes cyclooctene to the corresponding epoxide and MPL is quantitatively restored.

The catalytic epoxidation of olefins by Ph_4PHSO_5/MP may be considered a system of two consecutive processes, i.e. those of Eqs. (1–4) plus Eq. (5). Taking advantage of the information already collected on the oxo-forming process [9].

$$MPLO + Ol \overset{k_2}{\rightarrow} products \qquad (5)$$
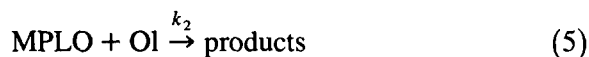
We have studied the olefin epoxidation, i.e. of the overall process, by measuring the rates of epoxide formation in 1,2-dichloroethane with three different olefins, i.e. cyclooctene, styrene and cis-stilbene at various substrate, oxidant, catalyst and imidazole concentrations. On the basis of the results obtained we suggest that the oxygen transfer from MPLO to the olefins does not necessarily involve an intermediate in spite of the fact that also in our system a saturation-like behavior is observed at large substrate concentrations.

2. Experimental section

2.1. Materials

1,2-Dichloroethane was purified by distillation over P_2O_5. Cyclooctene, styrene, cis-stil-

bene, the corresponding epoxides and imidazole were all commercially available, high purity, products, used as received. The preparation of Ph_4PHSO_5 (> 97%) has been previously reported [9]. Mn(TMP)Cl, has been prepared by using a slightly modified Lindsay–Smith method [11].

2.2. Kinetic methods

The quantitative analysis of the epoxides was carried out by GC on a Varian 3700 gaschromatograph equipped with a Varian CDS 401 integrator. 1,2-dibromobenzene was used as internal standard. 3% FFAP adsorbed on Chromosorb WAW DMCS was used as stationary phase for the 180 cm glass column. Typically, the reactions were initiated by adding 2 ml of a solution of Ph_4PHSO_5 in 1,2-dichloroethane to 3 ml of a solution in the same solvent containing the other components. The reaction vessel was thermostated at 0°C. Aliquots of the reaction mixture were withdrawn at the appropriate time internals, quenched with PPH_3 (or n-butyl sulfide when needed by the GC conditions) and analyzed. The concentrations and the experimental conditions used in the various runs are provided in the tables. Duplicate runs agreed within ±4%.

3. Results and discussion

The epoxidation reactions were run in 1,2-dichloroethane at 0°C. Ph_4PHSO_5, Mn(TMP)Cl and imidazole were the primary oxidant, the porphyrinato catalyst and the axial ligand, respectively. Three olefins, cyclooctene, styrene and cis-stilbene were epoxidized. Control experiments indicated that the epoxidation does not proceed in the absence of the catalyst. The presence of the axial ligand is also a necessary requisite. This confirms [9] that Ph_4PHSO_5 alone is not able to epoxidize olefins thus allowing us to neglect the contribution of the uncatalyzed process to the overall rate of oxidation. The lack of reactivity observed when imidazole is not added is in agreement with the results of our previous study [9] which showed that manganese–oxo-porphyrinato species, i.e. the real epoxidizing agent in solution, is not formed in the absence of the axial ligand. When Ph_4PHSO_5, Mn(TMP)Cl and imidazole are present, the epoxidation of the three olefins occurs.

Table 1

Values of k_{obs} for the epoxidation of 0.4 M cyclooctene and styrene in 1,2-dichloroethane at 0°C

Entry	Substrate	[Ph_4HSO_5] (M × 10^2)	[MnTMPCl] (M × 10^6)	[imidazole] (M × 10^2)	k_{obs} (10^4 s^{-1})
1	cyclooctene	2.0	0.5	2.0	0.5
2	cyclooctene	2.0	6.3	2.0	3.5
3	cyclooctene	2.0	29	2.0	20
4	cyclooctene	2.0	63	2.0	39
5	cyclooctene	1.0	6.3	2.0	3.8
6	cyclooctene	2.0	6.3	2.0	3.5
7	cyclooctene	4.0	6.3	2.0	3.7
8	cyclooctene	2.0	6.3	0.1	0.6
9	cyclooctene	2.0	6.3	0.2	1.5
10	cyclooctene	2.0	6.3	0.4	2.3
11	cyclooctene	2.0	6.3	1.0	3.5
12	styrene	2.0	6.3	0.1	1.0
13	styrene	2.0	6.3	0.2	1.4
14	styrene	2.0	6.3	0.5	1.6
15	styrene	2.0	6.3	1.0	2.5
16	styrene	2.0	6.3	2.0	3.5
17	styrene	2.0	6.3	5.0	3.5

By using pseudo-first-order conditions, i.e. an excess of the olefin over the oxidant, fair yields of epoxides are obtained. These range from 90 to 50% depending on the concentration of imidazole. In fact, a parallel oxidation of the ligand also takes place, which becomes significant at a large imidazole concentration. The product of cis-stilbene epoxidation is the cis-epoxide in agreement with the stereospecificity of the process observed also in previous studies [8]. The epoxidation rates were measured by determining at the appropriate time intervals the concentration of the epoxide formed. The corresponding rate constants were obtained from integrated pseudo-first-order plots, i.e. log([epox]$_\infty$ – [epox]$_t$) vs. time, which were linear up to 50% reaction. This suggests that the kinetic order of the oxidant is one. The rate law of the epoxidation is shown below (Eqs. (6), (7)):

$$R = d[epox]/dt = k_{obs}[Ph_4PHSO_5] \qquad (6)$$

$$k_{obs} = k_E[Ol]^x[Porph]^y[L]^z \qquad (7)$$

$$y = 1 \text{ and } 0 < x, z < 1$$

The k_{obs} values collected in Table 1 (entries 1–4) allow to establish that the kinetic order of the catalyst at a fixed cyclooctene, oxidant and imidazole concentration is also one. In fact a straight line with no intercept is obtained by plotting the pseudo-first-order rate constants as a function of Mn(TMP)Cl initial concentrations. Entries 5–7 of Table 1, referring to experiments carried out at different oxidant initial concentrations, confirm that the order in Ph$_4$PHSO$_5$ is one. Collected in Table 1 are the k_{obs} values obtained at a fixed cyclooctene, Ph$_4$PHSO$_5$ and catalyst concentration by increasing the axial ligand concentration. The rates increase reaching then a plateau at large imidazole/Mn(TMP)Cl ratios. By using the previously determined [9] values of the association constants of the two equilibria of Eqs. (1) and (2), one may calculate the ligand–porphyrin ratio at which MPL$_2$ is completely formed. Such a ratio is ca. 1.0×10^3 at 15°C. We find here, at 0°C, that the epoxidation rates become

Table 2
Values of k_{obs} for the epoxidation of three different olefins in the presence of MnTMPCl (6.3×10^{-6} M), imidazole (2.0×10^{-2} M) and tetraphenylphosphonium monopersulfate (2.0×10^{-2} M), in 1,2-dichloroethane at 0°C

Olefin	Concentration (M)	k_{obs} (10^4 s^{-1})
cyclooctene	0.1	2.7
cyclooctene	0.2	3.5
cyclooctene	0.4	3.5
cyclooctene	0.8	3.7
styrene	0.05	2.9
styrene	0.16	3.2
styrene	0.4	3.5
styrene	0.65	4.4
styrene	1.1	5.3
cis-stilbene	0.05	1.2
cis-stilbene	0.07	1.5
cis-stilbene	0.17	2.4
cis-stilbene	0.35	3.5
cis-stilbene	0.7	4.4
cis-stilbene	1.0	4.5

independent of imidazole concentration at a ligand–porphyrin ratio between 1 and 2×10^3. The relevant information provided by this circumstance is that the presence of the olefin has only a minor effect, likely due to the change of the properties of the solvent, on the equilibria leading to the formation of the mono- and biscoordinated porphyrinato–imidazole complexes. Moreover, also the oxygen transfers from Ph$_4$PHSO$_5$ to MPL and MPL$_2$ forming the oxo-manganese–porphyrinato complex MPLO appear to be only slightly affected by the presence of the olefin. This point, which is a very important one in view of the following discussion, has been further confirmed by the observation that the plateau occurs at similar concentration of ligand also when styrene, instead of cyclooctene, is epoxidized (Table 1). The data of Table 2 illustrate the change of the pseudo-first-order rate constants for the epoxidation of the three olefins (cyclooctene, styrene and cis-stilbene, respectively) as a function of olefin concentration. A plateau is reached for the three olefins. As mentioned in the introduction, this behavior suggested the occurrence of an intermediate oxo-manganese–porphyrin-olefin [7].
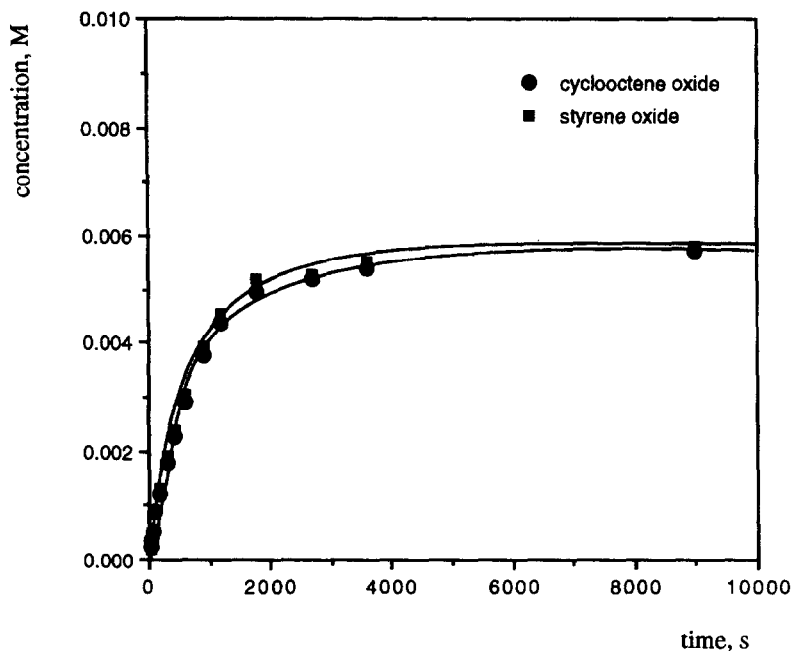
Fig. 1. Dependence of the epoxide concentration vs. time in a competitive experiment, involving 0.2 M cyclooctene and styrene at 0°C in DCE. Ph_4PHSO_5 = 0.02 M, MnTMPCl = 6.3 × 10⁻⁶ M, imidazole = 0.02 M.

Thus, one might conclude that a saturation of the oxo-species by the substrate is occurring as in Michaelis–Menten type kinetics. However, if this hypothesis is considered, one should also conclude that both the ability of the three olefins to coordinate to the oxo-species and the rates of
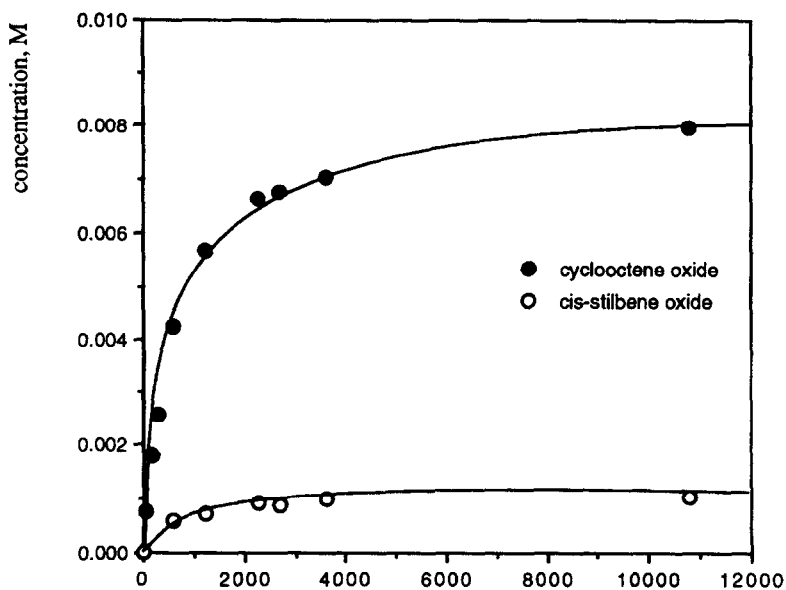

Fig. 2. Dependence of the epoxide concentration vs. time in a competitive experiment, involving 0.2 M cyclooctene and cis-stilbene at 0°C in DCE. Ph_4PHSO_5 = 0.02 M, MnTMPCl = 6.3 × 10⁻⁶ M, imidazole = 0.02 M.

the internal oxygen transfer to the double bond are very similar. In terms of Michaelis–Menten kinetics this means that both K_M and V_{max} for the three olefins should be similar. In particular, the similarity of the V_{max} values, i.e. the rates at the plateau, would imply that the internal oxygen transfer takes place at almost the same rate to rather differently substituted double bonds. This lack of selectivity is hardly rationalized on the basis of the different nucleophilic character of the three olefins and of their steric requirements. Furthermore, competitive experiments severely question such a conclusion. These are shown in Figs. 1 and 2. In particular two olefins were pitted together to compete against each other for the oxidant. The rate constants of the formation of cyclooctene oxide and of styrene oxide, measured in the competitive experiments, Fig. 1 are very similar, ca. 4×10^{-4} s^{-1} and also similar to those obtained in separate experiments (Table 2). This suggests that the two olefins do not compete. Following the same line of reasoning also cyclooctene and cis-stilbene do not compete (Fig. 2) since also in this case the rate constants measured in the competitive experiments, are ca. 4×10^{-4} s^{-1} again comparable with those measured in separate experiments. Surprisingly, however, the products distribution revealed by the data of Fig. 2 would suggest that cis-stilbene is at least 8-fold less reactive than cyclooctene.

In order to solve such a contradiction we suggest that in most of our experiments we are not measuring the rates of epoxidation but the rate of formation of the oxo-species. In particular, at low olefin concentration the oxygen transfer from the oxo-porphyrinato species MPLO to the olefin is relatively slow, so that the rates still depend on the olefin concentration, whereas, when larger amounts of substrate are added, the rate of formation of the oxo-species by reaction of MPL and MPL$_2$ with Ph$_4$PHSO$_5$ becomes the rate limiting step of the process. Of course the oxo-species is able to discriminate between cyclooctene and cis-stilbene as indicated by the products distribution

observed in the competitive experiments. On this basis the following reactivity order can be deduced: cyclooctene $\cong$ styrene $\gg$ cis-stilbene.

Under the experimental conditions employed in this investigation, the series of Eqs. (1–5) describing the various processes may be considerably reduced. In fact, the concentration of ligand L is large enough to safely assume that all the manganese–porphyrin is present as the bis-adduct MPL$_2$. This allows to neglect Eqs. (1), (2) and (3) by setting $[MPL_2] = [MP]_0$. From a kinetic point of view, the result of such a simplification is a system of the two consecutive reactions (4) and (5). Therefore, it is immediately evident that a zero-order dependence on olefin is expected if the rate of reaction (5) is larger than that of reaction (4). Such a situation may occur at large olefin concentration. For smaller excess of substrate a fractional order of the olefin is expected. The plausibility of our proposal may be directly tested. In fact, under our hypothesis, the rates measured at the plateaus, see Eq. (6), ranging in the interval $R = 8–10 \times 10^{-6}$ M s^{-1}, should roughly correspond to the rate of formation of MPLO which is ca. 6×10^{-6} M s^{-1} at 15°C in the absence of olefin [9]. The similarity of the two figures, obtained under different conditions, may be considered satisfactory. As a final comment, it should be pointed out that our data do not allow to rule out the presence of an intermediate. However, if such an intermediate is formed, this occurs after the rate limiting step of the process, when the concentration of olefin is sufficiently large, so that no kinetic information can be obtained of its presence.

4. Conclusions

The epoxidation of olefins by Ph$_4$PHSO$_5$ catalyzed by Mn(III)–porphyrinato complexes may be considered, under appropriate conditions, a system of two consecutive reactions. In the former, the oxo-manganese porphyrin is formed via an oxygen transfer from the oxidant

to the catalyst. In the latter reaction a second oxygen transfer takes place from the oxo-species to the olefin. If this reaction becomes fast owing to the large excesses of substrate used, the formation of the oxo-species may be the rate controlling reaction. Thus, a tendency towards a kinetic zero-order of the olefin cannot be taken as a firm evidence that the epoxidation reaction proceeds through the formation of an intermediate.

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