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A mechanistic study on oxidation of benzylic alcohols with PPh_4HSO_5 catalysed by manganese(III) porphyrins in homogeneous solution

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Abstract

The oxidation of variously ring-substituted 1-phenylethanols with Ph_4PHSO_5 catalysed by Mn(TMP)Cl and Mn(TDCPP)Cl in the presence of 4-*tert*-butylpyridine was studied in 1,2-dichloroethane homogeneous solution. The process leads only to C–H bond cleavage products, namely acetophenones. The oxidation rates are independent of the substrate concentration and, when Mn(TMP)Cl is the catalyst, even of the substrate nature. By increasing the concentration of 4-*tert*-butylpyridine, which acts as an axial ligand of the catalyst, a bell-shaped curve for the rate constants trend is observed. Hammett plots obtained by changing the substituents on the phenyl ring of the benzylic alcohol give different ρ values depending on the technique employed for rate constants determination, i.e., individual or competitive experiment. The observations reported above, together with a KIE of 2.5 in 1-D-1-phenylethanol oxidation measured by competitive experiment, are rationalised on the basis of a mechanistic scheme in which the oxo-manganese derivative is formed in the rate determining step of the catalytic process. Furthermore, it is suggested that alcohol dehydrogenation proceeds through a hydride abstraction involving an alcohol-oxo-porphyrinato complex.

Keywords: Oxidation; Peroxomonosulphate; Manganese; Porphyrins; Benylic alcohols

1. Introduction

Metalloporphyrins are known to catalyse the oxygenation of organic substrates with various oxygen donors, thus mimicking some of the transformations promoted by cytochrome *P*-450 enzymes [1–7]. The catalysis representing the shortened catalytic cycle of the enzyme involves reactions (1) and (2) of Scheme 1 [8–10], where M = Fe, Mn, Ru, etc.; X = Cl^-, ClO_4^-, AcO^-, pyridine, imidazole, etc.; P = porphyrin ring; O.D.(oxygen donor) = PhIO, RCO_3H, NaOCl, $KHSO_5$, etc.

The interaction between the oxygen donor and the metal centre of the catalyst forms a high valent metal oxo species which is the effective oxidising agent capable of transferring the oxygen atom to the substrate. A major task in determining reaction mechanism is to establish

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whether the oxygen transfer from the oxo metal porphyrin to the substrate (reaction 2 of Scheme 1) is a concerted or a two step process. From this point of view, alkane hydroxylation [11–14] and alkene epoxidation [15–20] are by far the reactions more extensively investigated. However, in spite of the impressive deal of mechanistic information now available, the mechanism of these processes is not yet unambiguously established and is still a matter of debate [21].

Much less information are available concerning another important chemical transformation promoted by both, cytochrome *P*-450 and synthetic metalloporphyrins, namely alcohol oxidation leading to carbonyl derivatives. Tabushi and Koga [22] first reported that manganese tetraphenylporphyrinate (MnTPPCl) catalyses benzyl alcohol oxidation to benzaldehyde by NaOCl in a biphasic medium. More recently, Labat and Meunier [23] and Wietzerbin et al. [24] investigated the oxidation of veratryl alcohol, 1,3-diols and tertiary diaryl alcohols with $KHSO_5$ catalysed by water soluble iron and manganese porphyrins as biomimetic models of ligninase. They found C–H and C–C bond cleavage products depending on the substrate nature and suggested the involvement of alkoxyl radicals as intermediate along the path leading to C–C cleavage. Baciocchi and Belvedere [25] focused the attention on the oxidation of secondary α-alkyl benzyl alcohols with PhIO catalysed by iron tetrapentafluorophenylporphyrinate (FeTPFPPCl) in which C–H and C–C bond cleavage can compete. They presented evidence suggesting that C–C bond cleavage products derive from the breakdown of an intermediate formed between the oxo iron species and the alcohol. Concerning the C–H bond cleavage products, it is suggested that a hydrogen atom abstraction followed by an oxygen rebound is taking place, similarly to the mechanism invoked in alkane hydroxylation.

$$\mathrm{MPX} + \mathrm{O.D.} \longrightarrow \mathrm{M(O)PX} \quad (1)$$

$$\mathrm{M(O)PX} + \mathrm{Sub} \longrightarrow \mathrm{MPX} + \mathrm{SubOx} \quad (2)$$

Scheme 1.

In the field of reactions promoted by metalloporphyrins, we have recently reported a study focused on ethylbenzene oxidation in a system which utilises tetraphenylphosphonium monopersulphate (Ph_4PHSO_5) and catalytic amount of a manganese porphyrin in the presence of a nitrogen base acting as axial ligand of the catalyst [26]. This system is particularly suitable for mechanistic studies which may be carried out under homogeneous conditions owing to the solubility of the oxygen donor in chlorined solvents such as 1,2-dichloroethane (DCE). In homogeneous conditions and at high axial ligand concentrations ($> 9.5 \times 10^{-2}$ M), a unitary kinetic order in substrate is observed, whereas by increasing the concentrations of the axial ligand at a fixed substrate concentration, a saturation behaviour is observed. These results together with the finding that chemioselectivity depends on the presence of nucleophiles and the low kinetic isotopic effect ($k_H/k_D = 2.7$) lead us to suggest that the hydroxylation proceeds through a concerted insertion of the oxo oxygen on the C–H bound rather than through a rebound mechanism. Since in our homogeneous oxidising system, the over oxidation of alcohol initially formed to ketone always represents a significant by-reaction, we became interested in studying the mechanism of the latter process in order to understand the factors which favour alcohol with respect to alkane oxidation. We wish now to present our results concerning the oxidation of variously substituted 1-phenylethanols with Ph_4PHSO_5 catalysed by manganese porphyrins, e.g., manganese 5,10,15,20-tetrakis(2′,4′,6′-trimethylphenyl)porphyrinate (MnTMPCl) and manganese 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrinate (MnTDCPPCl). The substrates investigated undergo only to C–H bond cleavage affording the corresponding ketones. The comparison between the kinetic behaviour of alcohols, reported in this paper, and alkanes previously reported, indi-

cates that two different mechanisms are operating.

2. Results and discussion

The oxidation of 1-phenylethanol with Ph_4PHSO_5 catalysed by Mn(TMP)Cl and Mn(TDCPP)Cl in the presence of 4-*tert*-butylpyridine acting as axial ligand of the catalyst in DCE at 30°C, has been examined. In this homogeneous system, the presence of an aromatic nitrogen base is essential for the formation of the oxo-manganese species which is the effective oxidant of the alcohol [27]. By using pseudo-first-order conditions, i.e., an excess of alcohol over Ph_4PHSO_5 and catalytic amount of manganese porphyrin respect with the oxidant, acetophenone yields ranging from low to fair are obtained, depending on the alcohol/axial ligand ratio. In fact, competitive pyridine oxidation takes place and becomes significant at large pyridine concentration. The oxidation rates were measured by determining by GLC analysis at the appropriate time intervals the concentration of acetophenone formed (internal standard method). The corresponding rate constants (k_{cat}) were obtained from integrated pseudo-first-order plots, i.e., $\log([\text{ketone}]_{t=8} - [\text{ketone}]_{t=t})$ vs. time, which were linear up to 80%–90% reaction. It should be noted that the rate constants obtained from the above mentioned calculation are composite quantities. In particular, they represent the summatory of the rate constants associated to all the parallel pseudo-first-order processes involving Ph_4PHSO_5. In the experimental conditions we adopted, the two major processes involving the oxidant are alcohol and 4-*tert*-butylpyridine oxidation. Therefore, the composite rate constant k_{cat} represents the addition of the first-order rate constants relative to alcohol (k_{OH}) and to 4-*tert*-butylpyridine (k_{py}) oxidation. The k_{OH} relative to alcohol oxidation can be numerically obtained simply multiplying the k_{cat} by the fractionary acetophenone yield.

Table 1 collects the results of some scout experiments aimed at establishing a suitable alcohol/pyridine ratio, capable of providing appreciable ketone yields.

Run 1, carried out in the absence of manganese porphyrin, shows that the stoichiometric oxidation of 1-phenylethanol by Ph_4PHSO_5 is a negligible reaction respect with the catalytic process. In the presence of catalyst but in absence of the aromatic nitrogen base (run 2), a faster reaction occurs with respect to the blank experiment. However, only when both the catalyst and pyridine are present does a fast catalytic alcohol oxidation take place (runs 3–6). In principle, this outcome is in agreement with two different mechanistic schemes. The first requires pyridine as necessary for promoting the formation of an oxo-manganese species, which oxidises the alcohol in a subsequent step. A second possibility is that Ph_4PHSO_5 itself can oxidise the alcohol coordinated to the manganese porphyrin. Accordingly to this hypothesis, pyridine acts as a base, assisting the alcohol

Table 1
Values of k_{cat}, k_{OH} and acetophenone yields relative to 1-phenylethanol oxidation with 2.0×10^{-2} M Ph_4PHSO_5 catalysed by 6.0×10^{-5} M Mn(TDCPP)Cl in the presence of 4-*tert*-butylpyridine, in DCE at 30°C

Run	1-Phenylethanol (M)	[4-*tert*-butylpyridine] $\times 10^3$ (M)	[OH]/[py]	$k_{cat} \times 10^3$ s^{-1}	Acetophenone yield (%)	$k_{OH} \times 10^3$ s^{-1}
1[a]	0.33	6.8	48.8	0.00042	nd	nd
2	0.33	–	∞	0.1	nd	nd
3	0.17	94.7	1.7	6.2	13.0	0.8
4	0.33	18.9	17.6	5.1	51.5	2.6
5	0.33	6.8	48.8	5.7	62.0	3.5
6	0.66	6.8	97.5	5.0	70.0	3.5

[a] In the absence of catalyst.

deprotonation and its coordination to the catalyst. However, this rationale has been ruled out on the base of control experiments which indicate a remarkable dependence of reaction rates on the steric hindrance of the aromatic nitrogen base. In particular, a strong base but a scarce nucleophile like 2,6-di-*tert*-butylpyridine revealed to be not effective in promoting alcohol oxidation by Ph_4PHSO_5 in the presence of Mn(TDCPP)Cl. This outcome suggests that pyridine coordination to the axial position of the catalyst plays a primary role rather than alcohol deprotonation. Runs 3–6 show that acetophenone yields increase with increasing the alcohol/axial ligand ratio, thus allowing us to minimise the parasite pyridine oxidation. Results of Table 1 provide information indicating, for alcohol oxidation, a different kinetic picture with respect to that found in alkane oxidation. In particular, runs 5,6 carried out at constant pyridine concentration and different alcohol concentrations indicate a kinetic zero order of substrate. Moreover, runs 4,5 carried out at constant alcohol concentrations but different pyridine concentrations indicate that the first-order rate constants (k_{OH}) increase with decreasing the axial ligand concentration. The hints provided by these preliminary experiments were confirmed by the oxidation carried out in the presence of Mn(TMP)Cl as the results of Table 2 show.

The most telling outcome of Table 2 is the following: whereas the kinetic order of substrate is zero at a fixed pyridine concentration (runs 8–11), the rate constant values depend on pyridine concentration in a non-monotonous way (runs 7,9,12). For comparison purposes, in Fig. 1, the dependence of the rate constants vs. axial ligand concentration in ethylbenzene and 1-

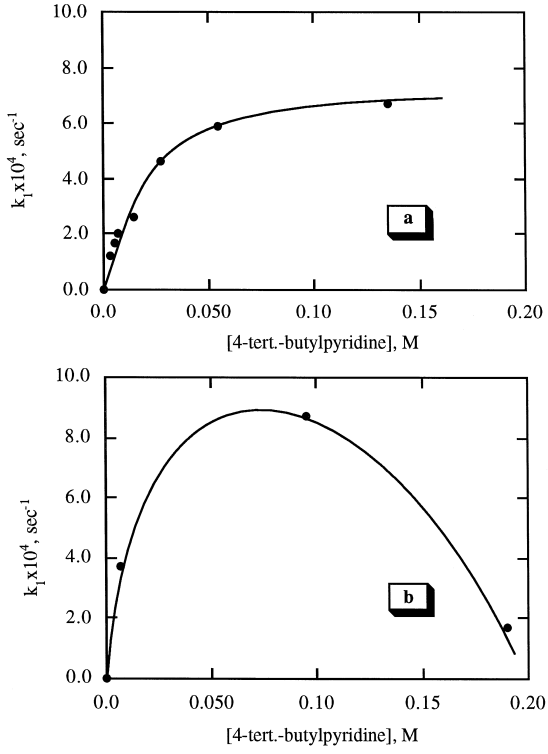


Fig. 1. Dependence of the rate constants vs. axial ligand concentration in oxidation of 0.33 M ethylbenzene (a) and 0.33 M 1-phenylethanol (b), with 2.0×10^{-2} M Ph_4PHSO_5 catalysed by 6.0×10^{-5} M Mn(TMP)Cl in the presence of 4-*tert*-butylpyridine, in DCE at 30°C.

Table 2
Values of k_{cat}, k_{OH} and acetophenone yields relative to 1-phenylethanol oxidation with 2.0×10^{-2} M Ph_4PHSO_5 catalysed by 6.0×10^{-5} M Mn(TMP)Cl in the presence of 4-*tert*-butylpyridine, in DCE at 30°C

Run	1-Phenylethanol (M)	[4-*tert*-butylpyridine] $\times10^3$ (M)	$k_{cat}\times10^3$ s^{-1}	Acetophenone yield (%)	$k_{OH}\times10^3$ s^{-1}
7	0.33	6.8	0.53	65	0.37
8	0.16	95	1.4	71	0.96
9	0.33	95	1.4	65	0.87
10	0.66	95	1.3	67	0.88
11	1.32	95	1.3	69	0.88
12	0.33	190	0.42	40	0.17
13	0.66	190	0.43	42	0.18
14	1.32	190	0.45	42	0.19

phenylethanol oxidation at a fixed substrate concentration is graphically shown.

When ethylbenzene is the substrate (Fig. 1a), the rate constants constantly increase, reaching then a plateau value at large pyridine/Mn(TMP)Cl ratios. A similar behaviour was also found in the oxidation of Mn(TMP)Cl to the corresponding oxo derivative, in the absence of organic substrate [27]. Both the situations can be rationalised by assuming a comparable reactivity toward Ph_4PHSO_5 of the mono- and bis-adduct formed between manganese porphyrin and nitrogen base. Thus, the saturation behaviour at large axial ligand concentrations simply reflects the increasing transformation of Mn(TMP)Cl into an 'effective catalyst' that is a species capable of generating the oxo-manganese-derivative, namely $Mn(TMP)Py^+$ and $Mn(TMP)Py_2^+$. Conversely, when 1-phenylethanol is the substrate, the rate constants increase with pyridine concentration till to a top value and then decrease with a further increase of pyridine concentration (Fig. 1b). The resulting bell-shaped profile should reflect two effects acting in opposite ways. The first one is the increasing concentration of the 'effective catalyst' which produces an increase of the measured rate constant values. The second effect, responsible for the rate constants drop, should be related with the intimate mechanism of alcohol oxidation. In particular, the rate constants decreasing at large pyridine/catalyst ratios indicates the association of the substrate to the 'effective oxidant' in a step preceding that leading to ketone. In fact, pyridine, which is necessary as axial ligand of the catalyst in order to promote the formation of the oxo-manganese species (the effective oxidant) [27], when present in large concentration may hamper alcohol coordination to the effective oxidant. In other words, the results of Table 2 are indicative of a Michaelis–Menten type mechanism in which the concentration of the reactive intermediate is determined even by pyridine concentration.

In order to gather further information on the intimate mechanism of alcohols dehydrogenation, the effect of a few substituents of 1-phenylethanols on oxidation rates has been studied. Thus, the reactivity order of four differently ring substituted 1-phenylethanols has been determined either by means of individual and competitive experiments. The pertinent results are collected in Tables 3 and 4, respectively.

The rate constants determined by individual experiments (Table 3), may be correlated in a Hammett plot with the appropriate sigma values (Fig. 2a).

The linear correlation is rather satisfactory for both the catalysts tested. Interestingly, whereas for Mn(TMP)Cl, the rate constants appear to be independent from the substituents present in the ring ($\rho = 0$), for Mn(TDCPP)Cl a ρ value of $+0.25$ is obtained. A ρ value near to zero could indicate a multi-step mechanism in which the rate determining step does not involve the substrate. In the process under investigation, the rate determining step should be the formation of the oxo-manganese derivative, which then oxidises the alcohol in a fast step. Incidentally, such a mechanistic picture could also account for the zero kinetic order of the substrate. On the other hand, it does not exclude an associative process for alcohol oxidation as suggested by the effect of axial ligand concentration on the rate constants. The small positive ρ value obtained in the oxidation catalysed by Mn(TDCPP)Cl ($\rho = +0.25$) is a rather unex-

Table 3
Oxidation of variously substituted 0.33 M 1-phenylethanols with 2.0×10^{-2} M Ph_4PHSO_5 catalysed by 6.0×10^{-5} M Mn(TMP)Cl and Mn(TDCPP)Cl in the presence, respectively, of 9.5×10^{-2} and 6.8×10^{-3} M 4-*tert*-butylpyridine, in DCE at 30°C

Run	Substrate	Catalyst	$k_{OH}\times10^3$ s^{-1}
15	1-phenylethanol	Mn(TMP)Cl	0.65
16	1-(4′CH_3-C_6H_4)ethanol	Mn(TMP)Cl	0.67
17	1-(4′Br-C_6H_4)ethanol	Mn(TMP)Cl	0.61
18	1-(4′NO_2-C_6H_4)ethanol	Mn(TMP)Cl	0.65
19	1-phenylethanol	Mn(TDCPP)Cl	1.18
20	1-(4′CH_3-C_6H_4)ethanol	Mn(TDCPP)Cl	1.07
21	1-(4′Br-C_6H_4)ethanol	Mn(TDCPP)Cl	1.44
22	1-(4′NO_2-C_6H_4)ethanol	Mn(TDCPP)Cl	1.81

Table 4
Competitive oxidation of variously substituted 0.33 M 1-phenylethanols with 2.0×10^{-2} M Ph_4PHSO_5 catalysed by 6.0×10^{-5} M Mn(TMP)Cl and Mn(TDCPP)Cl in the presence, respectively, of 9.5×10^{-2} and 6.8×10^{-3} M 4-*tert*-butylpyridine, in DCE at 30°C

Run	Substrates	Catalyst	k_X/k_H^a
23	1-phenylethanol + 1-(4′CH_3-C_6H_4)ethanol	Mn(TMP)Cl	1.37
24	1-phenylethanol + 1-(4′Br-C_6H_4)ethanol	Mn(TMP)Cl	0.90
25	1-phenylethanol + 1-(4′NO_2-C_6H_4)ethanol	Mn(TMP)Cl	0.24
26	1-phenylethanol + 1-(4′CH_3-C_6H_4)ethanol	Mn(TDCPP)Cl	1.28
27	1-phenylethanol + 1-(4′Br-C_6H_4)ethanol	Mn(TDCPP)Cl	0.89
28	1-phenylethanol + 1-(4′NO_2-C_6H_4)ethanol	Mn(TDCPP)Cl	0.44

[a]The ratios k_X/k_H are obtained by dividing the concentration of ketone originated from the substituted (4′X-C_6H_4)1-phenylethanol by the concentration of acetophenone originated from 1-phenylethanol.

pected result which needs a comment. In fact, the oxo-manganese derivative is known to be an electrophilic oxidant, thus reacting easier with electron-rich substrates [1–7]. On the contrary, we observe in the presence of Mn(TDCPP)Cl, a slightly faster reaction with relatively electron-poor substituted 1-phenylethanols. A possible rationale for this outcome takes into account the feature of the oxygen transfer from the oxygen donor to the manganese porphyrin and suggests that it could be affected by the nature of the substrate. This hypothesis relays on the fact that the anionic monopersulphate is a rather poor electrophilic oxidant. In fact, it is unable to oxidise the manganese porphyrin in the absence of a basic axial ligand whose role is to improve the oxidazibility of the metal centre [27]. However, the net negative charge of monopersulphate can be reduced by specific solvation provided by a good proton donor for hydrogen-bonding. The increasing electron-withdrawing character of substituents in the 1-phenylethanol ring favours the hydrogen bonding between the alcoholic proton and the anionic peroxidic oxygen, thus making the oxygen donor a more efficient electrophilic oxidant. Consequently, the rate determining step, i.e., the oxo-manganese formation, becomes faster in the presence of *p*-nitro with respect to *p*-methyl-1-phenylethanol. Furthermore, the dependence of rate formation of the oxo-manganese species on the substrate nature should manifest more when Mn(TDCPP)Cl is the catalyst, owing its electron-poor manganese centre comparatively to that of Mn(TMP)Cl. In Fig. 2b, the Hammett plot obtained by competitive experiments in which substituted 1-phenylethanols were pitted against 1-phenylethanol to compete for the 'effective oxidant' (Table 4) is shown. In these

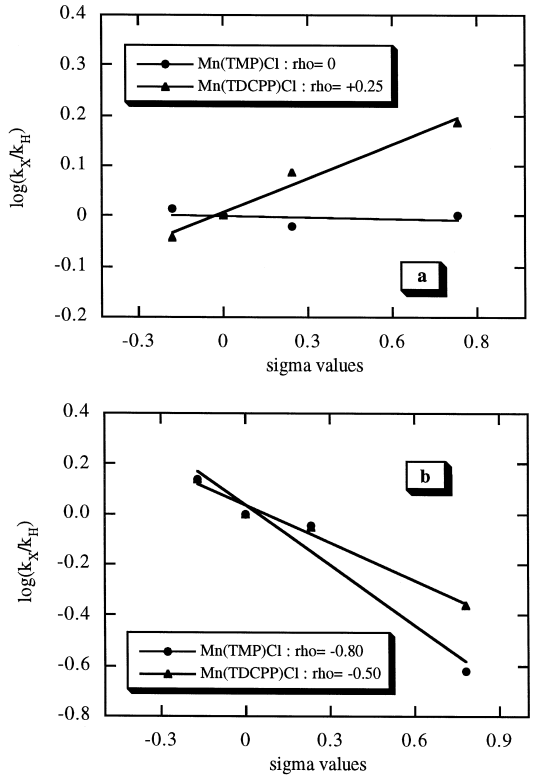


Fig. 2. Hammett plots for the oxidation of 0.33 M substituted 1-phenylethanols carried out by individual (a) and competitive (b) experiments, with 2.0×10^{-2} M Ph_4PHSO_5 catalysed by 6.0×10^{-5} M Mn(TMP)Cl (●) and 6.0×10^{-5} M Mn(TDCPP)Cl (▲), in the presence, respectively, of 9.5×10^{-2} and 6.8×10^{-3} M 4-*tert*-butylpyridine, in DCE at 30°C.

experiments, the relative rate constants are evaluated by measuring the products ratio when all the oxidant was consumed. It may be noted that also in this case the linear correlation is quite satisfactory. However, the picture is radically different from that obtained by individual experiments. In fact, for both the catalysts tested, namely Mn(TMP)Cl and Mn(TDCPP)Cl, negative ρ values of, respectively -0.80 and -0.50, are observed. This outcome strongly supports the hypothesis of a rate-determining step involving the formation of the oxo-manganese derivative. In fact, in the competitive experiments, even if the oxygen transfer from monopersulphate to the catalyst is the rate-determining step, the oxo-species being formed can discriminate between the two alcohols accordingly to the electronic requirements of the oxidative process. Therefore, a negative ρ value is observed, indicating that the oxo-manganese derivative normally behaves as the electrophilic partner in the oxidative process. Such a general mechanistic scheme is further supported by the kinetic isotope effect in the oxidation of 1-phenylethanol and 1-D-1-phenylethanol measured by both individual and competitive techniques. Table 5 collects the pertinent data.

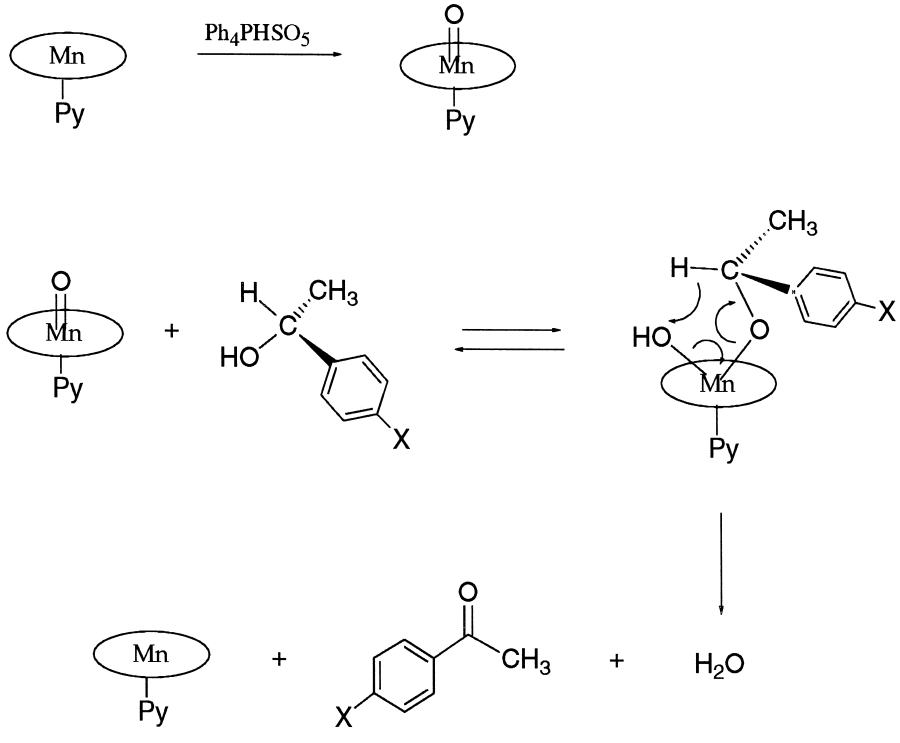
Runs 29 and 30 of Table 5 show that 1-phenylethanol and its isotopically marked derivatives react at the same rate, thus determining a unitary KIE. This outcome suggests that hydrogen abstraction from the α carbon of alcohol occurs during a fast step of the catalytic process and fits with the proposal of the oxo-derivative formation as rate determining step. Although in these experiments, Mn(TDCPP)Cl was employed as catalyst, even small differences in the rate constants of the two substrates were not detected, thus indicating that the effect of hydrogen bonding capability of 1-phenylethanol and its isotopically marked derivative on the rate of oxo-manganese species formation is negligible. The oxo-manganese formation in a slow step precludes the possibility of checking the existence of a KIE during the alcohol dehydrogenation step simply by measuring the rate constants of the two substrates through individual experiments. However, also in this case competitive experiments can be of help. Of course, it is not possible to evaluate the KIE simply by reacting together 1-phenylethanol and 1-D-1-phenylethanol because acetophenone is formed in both reactions. In this case, two competitive experiments with a third reference substrate are needed. In the first experiment, 1-phenylethanol and the reference substrate are pitted together to compete for the oxidant and the ratio $k_{\text{1-phenylethanol}}/k_{\text{reference substrate}}$ is obtained from the products ratio. In the second experiment, 1-D-1-phenylethanol is pitted together with the reference substrate to compete for the oxidant and the ratio $k_{\text{1-D-1-phenylethanol}}/k_{\text{reference substrate}}$ is obtained. Finally, the $k_{\text{1-phenylethanol}}/k_{\text{1-D-1-phenylethanol}}$ reactivity ratio is obtained by dividing $k_{\text{1-phenylethanol}}/k_{\text{reference substrate}}$ by $k_{\text{1-D-1-phenylethanol}}/k_{\text{reference substrate}}$. Cumene was selected as reference substrate for two main reasons. First, hydrocarbon hydroxylation in our homogeneous oxidising system does not appear to proceed through substrate coordination to the

Table 5
Oxidation of 0.33 M 1-phenylethanol and 0.33 M 1-D-1-phenylethanol in individual experiments and in competitive experiments with 0.33 M cumene, with 2.0×10^{-2} M Ph_4PHSO_5 catalysed by 6.0×10^{-5} M Mn(TDCPP)Cl in the presence of 6.8×10^{-3} M 4-*tert*-butylpyridine, in DCE at 30°C

Run	Substrates	$k_{OH}\times10^3$ s^{-1}	[Acetophenone]$t=\infty$ [cumylalcohol]$t=\infty$	k_H/k_D
29	1-phenylethanol	1.2	–	
30	1-D-1-phenylethanol	1.2	–	1.0
31	1-phenylethanol + cumene	–	10.0	
32	1-D-1-phenylethanol + cumene	–	4.0	2.5

catalyst, thus avoiding interferences with alcohol association to the oxidant. Furthermore, tertiary cumyl alcohol formed does not undergo further reaction, making simpler the oxidation process. Runs 31 and 32 allow to evaluate a KIE of 2.5 in 1-phenylethanol oxidation. Such a value clearly indicates that hydrogen abstraction from the α carbon occurs in the rate-determining step of alcohol oxidation. Concerning the intimate mechanism of carbon–hydrogen bond breaking, conclusive results are not yet available. However, on the basis of the data collected, the mechanism shown in Scheme 2 seems reasonable.

According to the proposed mechanism, the oxo-manganese species is formed in the r.d.s. of the catalytic process. Furthermore, alcohol coordinates the oxo-derivative in a subsequent reversible way; this assumption is required by the fact that pyridine exercises an inhibitory effect on alcohol oxidation rates. The resulting intermediate should involve a seven-coordinate manganese in which the porphyrin ring cannot be in the same plane as the metal. Seven-coordinate iron species have been observed in a number of complexes [28] and it is known that the metal centre in porphyrin complexes may move up to the porphyrin plane, even in the case of six-coordinated complexes [29]. In the subsequent rate determining step of alcohol oxidation, the hydrogen atom is transferred from the α carbon atom to the hydroxo group while the manganese centre is reduced to the native Mn(III). The last step resembles that occurring in chromate oxidation of alcohols [30] and formally consists in a hydride transfer which leaves a fractionary positive charge on the alcoholic α carbon. The development of such electron deficiency on the substrate in the transition state of alcohol oxidation fits satisfactorily with the negative ρ values measured in competitive experiments. As an additional comment, it may be noted that the absolute ρ values are rather small, thus suggesting that hydride transfer and the formation of



Scheme 2.

carbonyl double bond take place with a certain degree of syncronicity. The KIE value measured in the oxidation of 1-phenylethanol and 1-D-1-phenylethanol, indicates that the cleavage of the carbon–hydrogen bond leading to acetophenone occurs in a slow step. Moreover, its relatively modest value ($k_H/k_D = 2.5$) appears to be more in agreement with a non-symmetric transition state as that involved in hydride transfer rather than that occurring in a hydrogen abstraction–recombination mechanism. In fact, when the latter mechanism is operating, large KIE (> 10) are normally observed [31].

3. Conclusions

The present kinetic study allowed to establish the general mechanistic scheme for alcohol oxidation with Ph_4PHSO_5 catalysed by manganese porphyrins in homogeneous solution. In particular, it has been shown that the formation of an oxo-manganese species is the rate determining step of the catalytic process. Moreover, evidence has been collected suggesting that r.d.s can be affected by hydrogen bonding involving the alcoholic substrate and anionic monopersulphate. Such interactions determine the oxidising ability of the oxygen donor and reflect on the rate formation of the effective oxidant. From the inhibitory effect of pyridine concentration on oxidation rates, we inferred the alcohol coordination to the effective oxidant. Concerning the intimate mechanism of alcohol oxidation, we collected some information by means of competitive experiments. Hammett's ρ values and the KIE suggest that hydrogen abstraction occurs in a slow step, leaving a positive charge on the alcoholic α carbon.

Although these results cannot be considered conclusive in pointing at a definite mechanism, it seems reasonable that a picture in which a hydride abstraction is taking place, be similar to that observed in aliphatic alcohol oxidation performed by the oxo functionality of chromate. Thus, alcohol oxidation by oxo-manganese species appear to proceed through a dehydrogenation mechanism rather than through an alcohol hydroxylation followed by the loss of water leading to ketone.

4. Experimental section

4.1. Materials

DCE was purified by distillation over P_2O_5. Cumene was purified by distillation over $NaBH_4$. Tetramesitylporphyrin ($TMPH_2$) and 2,6-dichlorophenylporphyrin ($TDCPPH_2$) were synthesised following a slightly modified Lindsay-Smith method [32,33]. The metallation of $TMPH_2$ and $TDCPPH_2$ with $Mn(II)(OAc)_2$ was performed by conventional methods [34,35]. Ph_4PHSO_5 was prepared and purified as previously reported [27]. Oxone, tetraphenylphosphonium chloride, bromobenzene (GLC internal standard), 4-*tert*-butyl pyridine, 1-phenylethanol were all commercially available, high purity products (Aldrich) were used as received. 1-(4′NO_2-phenyl)ethanol, 1-(4′Br-phenyl)ethanol, 1-(4′CH_3-phenyl)ethanol and 1-D-1-phenylethanol were prepared from the corresponding ketone by reduction with $NaBH_4$ or $NaBD_4$ in refluxing ether and purified by chromatography (silica gel, dichloromethane).

4.2. Kinetic measurements; single reactions

Typically, the reactions were initiated by adding 2 ml of a DCE solution containing 0.10 mmol of Ph_4PHSO_5 (solution A) to a 3-ml DCE solution containing 3.1×10^{-4} mmol of Mn(TMP)Cl, 4×10^{-2} mmol of internal standard, 0.47 mmol of 4-*tert*-butylpyridine (axial ligand) and 1.6 mmol of substrate (solution B), in a jacketed reactor thermostated at 30°C. At appropriate time intervals, 0.10 ml of reaction mixture were withdrawn, quenched with an equivalent volume of a 0.4-M solution of PPh_3 in DCE and analysed by GLC analysis. Duplicate

runs agreed within ±5% which can be considered the error of the rate constants.

4.3. Kinetic measurements; competitive reactions

Competitive reactions were performed following the general above described procedure with the exception that solution B contains 1.6 mmol of each substrate. Relative rate constant of substrate 2 with respect to substrate 1 was determined by dividing the product concentrations measured by GLC analysis.

4.4. Instruments

The concentrations of the products in the oxidation of 1-phenylethanols and cumene were determined by GLC analysis with the internal standard method on the basis of previously calculated response factors. The analyses were performed on a 10% Carbowax 20 M, adsorbed on Chromosorb WAW-DMCS 80/100 (1.8 m glass column). The GC was a Varian 6000 equipped with a Shimadzu C-R4 A data processor. The identification of the reaction products was performed by GLC comparison with authentic samples and/or by GC-MS analysis carried out with a Hewlett-Packard 5890 gaschromatograph, connected with a Hewlett-Packard 5970 mass selective detector, using a 15-m SE-30 capillary column, 0.25 mm i.d.

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