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Journal of Molecular Catalysis A: Chemical 130 (1998) 221–231

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Oxidation of alkanes by Ph_4PHSO_5 catalyzed by manganese(III) porphyrins. A study of the factors determining alcohol and ketone formation

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Received 15 July 1997; accepted 2 October 1997

Abstract

As reported in previous papers, the oxidation of ethylbenzene with Ph_4PHSO_5 catalyzed by Mn(TMP)Cl in the presence of nitrogen bases in 1,2-dichloroethane homogeneous solution affords fair yields (up to 80%) of oxygenated products. Acetophenone is the major product together with minor amounts of 1-phenylethanol ([ketone]/[alcohol] ≅ 6). In this paper we report further observations concerning this system. In particular we find that a similar products distribution is observed when soluble Co(II) or Fe(II) species, i.e. acetylacetonate derivatives, are used instead of the manganese porphyrin. On the other hand for these compounds, which are catalysts of radical reactions, the product distribution is determined by a remarkably larger reactivity of the alcohol initially formed compared with that of the alkane ($k_{R-OH}/k_{R-H} \cong 200$). The product distribution for the Mn(TMP)Cl catalysis cannot be rationalized on the same basis. Direct experiments show that the reactivity of the two substrates is similar ($k_{R-OH}/k_{R-H} \cong 2$–6) thus suggesting that a mechanism different from the simple radical hydrogen atom abstraction is taking place. The dependence of the chemioselectivity of hydrocarbon oxidation on the nature of the manganese porphyrin employed and of a number of additives indicates that the product distribution is mainly determined by the relevance of the association of the alcohol intermediate to the catalyst prior to the second oxidation step leading to ketone. Two different rho Hammett's values are obtained for ethylbenzenes oxidation depending on the method employed for the measurement of reaction rates, i.e. by separate or by competitive experiments thus providing further mechanistic information on the association of the substrates to the oxo-species. © 1998 Elsevier Science B.V.

Keywords: Alkanes; Hydroxylation; Oxidation; Manganese; Porphyrins; Peroxomonosulfate

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1. Introduction

We have previously reported [1] that in the oxidizing system which utilizes tetraphenylphosphonium monopersulfate (Ph_4PHSO_5) and catalytic amounts of 5,10,15,20-tetrakis(2′,4′,6′-trimethylphenyl)porphyrinate (Mn(TMP)Cl) under homogeneous conditions in 1,2-dichloroethane (DCE) in the presence of a nitrogen base as axial ligand of the catalyst, the oxidation of ethylbenzene affords

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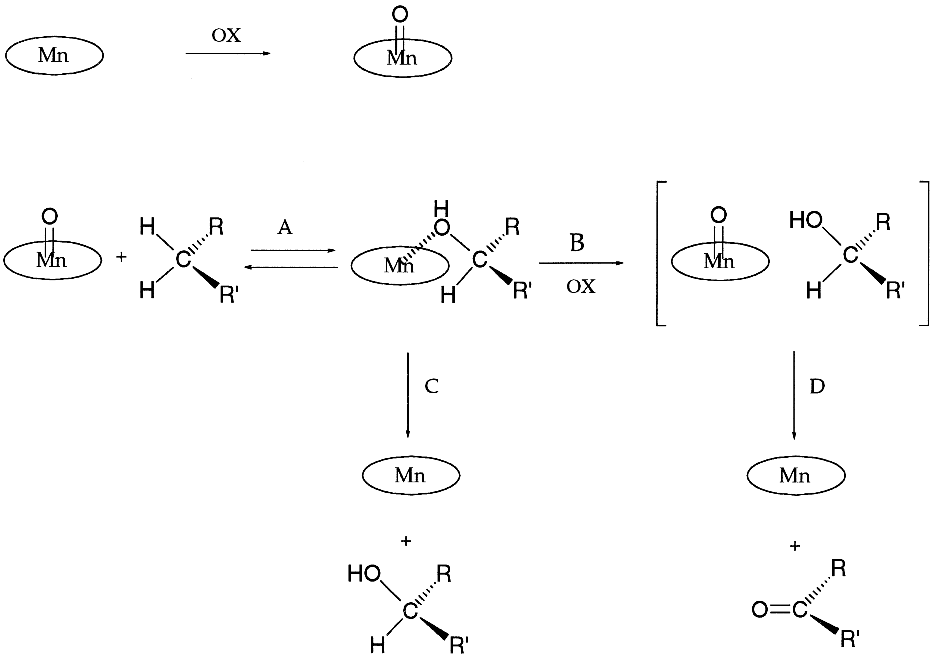
PII S1381-1169(97)00222-7



Scheme 1.

mainly acetophenone together with minor amounts of 1-phenylethanol. The similarity between the rate of appearance of the ketone and of the alcohol led us to suggest the occurrence of two parallel rather than two consecutive processes. Moreover, in the rate law of the reaction, the kinetic order of the substrate is less than one (0.4–0.7) even at the lowest concentrations employed [1]. We rationalized this observation (see Scheme 1) by assuming the occurrence of equilibrium A largely shifted to the right to form an oxo-porphyrinate–substrate complex.

An alternative rationale, i.e. the rate limiting formation of the oxo-porphyrinate species followed by faster processes leading to products appears to be ruled out by the fact that different substrates react at different rates. In particular, a much higher reactivity of olefins compared with that of alkanes and alcohols, under similar experimental conditions, is observed [1,2].

The equilibrium formation of the oxo-porphyrinate–substrate intermediate complex allows the rationalization of the peculiar chemioselectivity observed, i.e. the predominant ketone formation. In fact, as suggested in Scheme 1, the evolution of such a complex in the presence of an excess of Ph_4PHSO_5 leads to a new oxo-derivative in which the incipient alcohol formed, still within the coordination sphere of the metal (steps B, D), is oxidized. As a consequence, the alcohol produced comes from a minor pathway, i.e. the process which liberates free alcohol in solution (step C). The mechanistic picture summarized above, though reasonable, is indeed a speculative one which needs corroboration by more experimental data, particularly as far as the intimate process of the oxygen transfer from the oxo-derivative to the aliphatic C–H bond is concerned. Therefore, we have continued our investigation and in this paper we report an examination of the factors which affect the chemioselectivity of alkane oxidation promoted by manganese porphyrins. Furthermore, we present the results of a kinetic study aimed at comparing the various oxidation rates and the chemioselectivites of various oxidizing systems including those whose mechanistic features are well established. In particular, we compare our model system, i.e. Mn(TMP)Cl/pyridine/Ph_4PHSO_5, with the typical radical oxidizing systems based on Co(II) or Fe(II) catalysts [3] and with the system Mn(TMP)Cl–Ph_4PHSO_5 in the presence of benzoates [4,5] as axial ligands which also has shown radical features. The results collected suggest a non-radical nature of the oxygen insertion into the aliphatic C–H bond.

2. Results and discussion

The oxidation of ethylbenzene with Ph_4PHSO_5 catalyzed by Mn(TMP)Cl in the presence of 4-*tert*-butylpyridine in DCE at 30°C has been examined. The oxidation rates were measured by determining by GLC analysis (internal standard), at the appropriate time intervals, the concentration of acetophenone and 1-phenylethanol formed. The corresponding rate constants were obtained from integrated pseudo-first order plots, i.e. $\ln([\text{ketone}]_\infty - [\text{ketone}]_t)$ versus time linear up to 50% reaction. The ratios [ketone]/[alcohol] were determined at the end of the reaction i.e. when the concentrations of the two products have reached a constant value corresponding to 50–80% yield based on the oxidant.

In Table 1 kinetic data for ethylbenzene oxidation in the presence of various additives which may act as competitors of the alcohol initially formed [5–8] are shown.

In our previous work [1] we had observed that by increasing the concentration of the nitrogen base the chemioselectivity of the oxidative process was modified. In particular, more alcohol was formed. A drop of the overall yield due to the competitive axial ligand oxidation was also observed. Here, variations of selectivity are not accompanied by diminution of the yields (see entries 1–3 of Table 1) because of the presence of added water which removes part of the initially formed alcohol from the coordination sphere of the metal without being oxidized. The limited solubility of water in DCE, however, makes it difficult to force the reaction toward the almost exclusive alcohol production by acting on the competitor concentration.

Thus, we examined the effect of competitors more soluble than water. Entries 4 and 5 show the effect of *tert*-BuOH on ethylbenzene oxidation.The ketone/alcohol ratio does change, though to a smaller extent than that expected. In addition the overall yield increases up to 86%. Acetophenone remains the main product. The rather small effect exhibited by *tert*-BuOH probably depends on its scarce nucleophilicity. In fact, a much more pronounced effect of the competitor on chemioselectivity is found in the case of the more acidic MeOH (entries 6–9). Thus, in the presence of 5.0 M added

Table 1
Oxidation of 0.65 M ethylbenzene by 2.0×10^{-2} Ph_4PHSO_5 M catalyzed by 6.0×10^{-5} M Mn(TMP)Cl in the presence of 9.5×10^{-2} M 4-*tert*-butylpyridine and various additives, in DCE, at 30°C

Entry	Solvent	Additive, M	$k_{\text{obs.}}$(ketone), $\times 10^4$ (s^{-1})	Yield (%)	[ketone]/[alcohol]
1	DCE	—	6.4	55	6
2	DCE[a]	H_2O	10.4	52	4.6
3	DCE[b]	H_2O	14.8	73	3.7
4	DCE	*tert*-BuOH, 2.0	4.8	86	3.2
5	*tert*-BuOH	—	4.4	63	2.1
6	DCE	MeOH, 0.25	7.8	50	4
7	DCE	MeOH, 2.0	2.2	49	2.3
8	DCE	MeOH, 5.0	1.0	36	1.4
9	MeOH	—	n.d	3	0.35

[a] DCE was saturated with H_2O.
[b] The reaction was carried out in a two phase system, 5 ml DCE, 1 ml H_2O.

Table 2
Oxidation of 0.6 M ethylbenzene and 0.6 M 1-phenylethanol by 2.0×10^{-2} M Ph_4PHSO_5 promoted by various 6.0×10^{-5} M catalysts, in DCE at 30°C

Entry	Substrate	Catalyst	$k_{obs.}$(ketone) $\times 10^4$ (s^{-1})	[ketone]/[alcohol]
1	ethylbenzene	Mn(TMP)Cl	6.4	6
2	ethylbenzene	Mn(TDCPP)Cl	1.7	0.3
3	1-phenylethanol	Mn(TMP)Cl	8.8	∞
4	1-phenylethanol	Mn(TDCPP)Cl	14.0	∞
5	ethylbenzene	$Co(acac)_2$	0.2	4
6	1-phenylethanol	$Co(acac)_2$	38.3	∞

methanol, acetophenone and 1-phenylethanol are formed in comparable amounts. In methanol, the latter product becomes the predominant one. In this case however, the overall yield drops, probably because of the concomitant solvent oxidation [6–8]. Further evidence supporting the importance of alcohol coordination to the manganese porphyrin in determining the chemioselectivity of hydrocarbon oxidations is provided by the results reported in Table 2.

The comparison of the data of entries 1–4 of Table 2 concerning the reactivity of ethylbenzene and 1-phenylethanol with two catalysts, Mn(TMP)Cl and 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphyrinate (Mn(TDCPP)Cl), indicates that even though reactivity ratios alcohol/hydrocarbon for Mn(TDCPP)Cl and Mn(TMP)Cl of 8.0 and 1.4, respectively, are found, the [alcohol]/[ketone] ratios are still in the order Mn(TMP)Cl > Mn(TDCPP)Cl. These results confirm that the chemioselectivity of hydrocarbon oxidation catalyzed by manganese porphyrins is little affected by the intrinsic reactivity of the substrates whereas a major role is played by the occurrence of an alcohol–catalyst association. Fig. 1 shows the behavior of the appearance of the products in ethylbenzene oxidation by Ph_4PHSO_5 catalyzed by Mn(TMP)Cl and the simulated kinetic profile for the same process according to Scheme 2 in which the ketone formation is described as the result of two consecutive reactions.

In the simulated curves of Fig. 1 a k_3/k_2 value of 6.1 has been imposed. This is the value determined by competitive experiments as will be discussed later (see Table 5). Such a reactivity ratio is larger than that found by separate experiments which gave k_3/k_2 ca. 2.0. At any rate, even by using the k_3/k_2 value of 6.1, the simulated products ratio at the end of the reaction is still the opposite than that experimentally found. On passing, it may be mentioned that in the simulated kinetic

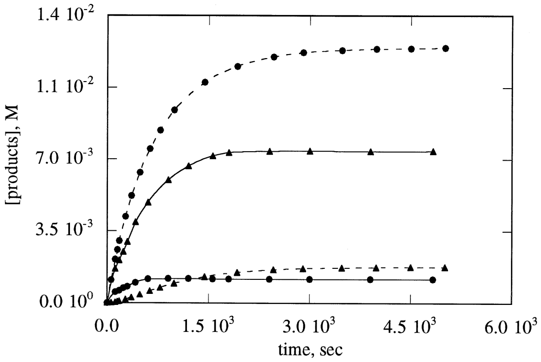


Fig. 1. Appearance of acetophenone (▲) and 1-phenylethanol (●) as a function of time in the oxidation of 0.6 M ethylbenzene with 2.0×10^{-2} M Ph_4PHSO_5 catalyzed by 6.0×10^{-5} M Mn(TMP)Cl in the presence of 2.7×10^{-3} M 4-*tert*-butylpyridine, in DCE, at 30°C, as experimentally determined (————) and simulated (- - -) according to Scheme 2 (see text) in which $k_1 = 21$, $k_2 = 100$, $k_3 = 610$.

$$\mathrm{OD} + \mathrm{MP} \xrightarrow{k_1} \mathrm{OMP} + \mathrm{D}$$

$$\mathrm{OMP} + \mathrm{R_1R_2CH_2} \xrightarrow{k_2} \mathrm{R_1R_2CHOH}$$

$$\mathrm{OMP} + \mathrm{R_1R_2CHOH} \xrightarrow{k_3} \mathrm{R_1R_2C{=}O}$$

Scheme 2.

profiles the final products ratio depends only on k_3/k_2 ratio while the k_2/k_1 ratio determines the shape of the curves and the observed rate constant value. The simulated curves of Fig. 1 were obtained by using a k_2/k_1 value of 4.9. This is the value which best reproduces the rate constants experimentally found. The outcome of this simulation is that ketone production in the hydrocarbon catalyzed oxidation studied here cannot be the result of two simple consecutive reactions.

A product distribution similar to that observed with Mn(TMP)Cl is also found when Co(acac)$_2$ is the catalyst (entries 5–6). In this system the actual oxidizing agent is assumed to be the radical $SO_4^{-}\cdot$ [9] so that the ratio [ketone]/[alcohol] ≅ 4 is likely due to the much higher reactivity of such radical toward the alcohol. This is confirmed by the experimental finding that the alcohol reacts 200 fold faster than the hydrocarbon, (see Tables 2 and 5). In this case, in Scheme 2 Co(acac)$_2$ replaces Mn(TMP)Cl and $SO_4^{-\cdot}$ replaces Mn(O)TMP.

The difference of the two systems examined, Co(II)/HSO_5^- and Mn(Porph.)/HSO_5^-, namely the much larger reactivity of the alcohol in the former, suggests that two different mechanistic pathways are operating even if a similar products distribution is observed. In particular, since the oxidation carried out by $SO_4^{-\cdot}$ is a radical process involving a hydrogen atom abstraction from the substrate, it seems rather unlikely that the oxo-manganese porphyrinate becomes involved in a radical pair formation contrary to what is commonly accepted for hydrocarbon hydroxylation catalyzed by iron porphyrins [10–20]. Fig. 2 shows that the peculiar chemioselectivity in alkane oxidation promoted by Mn(TMP)Cl/pyridine can be accommodated within the general mechanistic Scheme 3.

In fact, the kinetic profile, the products ratio and the observed rate constants obtained by calculations on the basis of Scheme 3 agree with the experimental data (see Fig. 2). Fig. 2 was obtained by using the following values: $k_1 = 32\ \mathrm{M^{-1}\ s^{-1}}$, $k_2 = 100\ \mathrm{M^{-1}\ s^{-1}}$, $k_3 = 32\ \mathrm{M^{-1}\ s^{-1}}$,

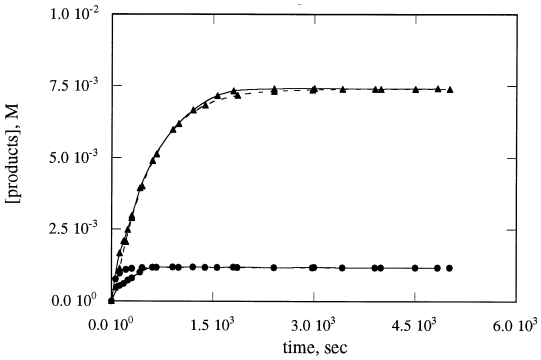
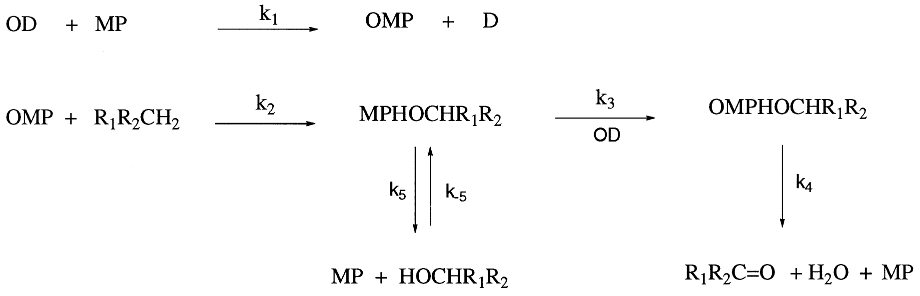


Fig. 2. Appearance of acetophenone (▲) and 1-phenylethanol (●) as a function of time in the oxidation of 0.6 M ethylbenzene with 2.0×10^{-2} M Ph_4PHSO_5 catalyzed by 6.0×10^{-5} M Mn(TMP)Cl in the presence of 2.7×10^{-3} M 4-*tert*-butylpyridine, in DCE, at 30°C, as experimentally determined (————) and simulated (- - -) according to Scheme 3 (see text) in which $k_1 = k_3 = 32$, $k_2 = k_4 = k_5 = 100$, $k_{-5} = 85000$.



Scheme 3.

$k_4 = 100$ M^{-1} s^{-1}, $k_5 = 100$ M^{-1} s^{-1}, $k_{-5} = 85000$ M^{-1} s^{-1}. In Scheme 3 the intrinsic reactivity of the hydrocarbon and that of the alcohol toward the oxo-manganese porphyrin is provided, respectively, by k_2 and k_4 values. A larger ketone versus alcohol production is achieved by imposing a large value of the equilibrium constant relative to alcohol–catalyst intermediate formation. In such a way it is possible to reverse the chemioselectivity which, in the absence of such an intermediate, would favor alcohol accumulation owing to the large excess of the hydrocarbon over the oxidant and to the fact that k_2 and k_4 are similar.

In order to address the problem of the intimate oxygen transfer mechanism, the effect of the substituents of the hydrocarbon on the oxidation rates has been studied. Thus, the reactivity order of four variously ring substituted ethylbenzenes has been determined either by means of competitive or independent experiments. The pertinent results are collected in Tables 3 and 4, respectively.

The results obtained from the oxidation carried out on the single substrates (Table 3) may be correlated in a Hammett plot with the appropriate sigma values (Fig. 3).

In spite of the limited number of points available, the linear correlation is rather satisfactory ($R = 0.99$). A rho value of -0.31 is obtained. Interestingly, a clear trend of the chemioselectivity of the process is also observed. In particular, ketone production increases with increasing the electron-withdrawing character of the substituent in the ring. This suggests that the ketone is originated by an intermediate in which the alcohol as such rather than its alcoholate form is coordinated to the catalyst. In the latter case in fact, an opposite trend should have been observed.

In Fig. 3 is also shown the Hammett plot obtained by competitive experiments in which substituted ethylbenzenes were pitted against ethylbenzene to compete for the catalyst (Table 4). It may be noted that also in this case the linear correlation is quite satisfactory ($R = 0.99$). However, the resulting rho value (-0.78) is considerably larger than that obtained by individual experiments. The sign is the same. Both absolute values are rather small. The fact that different rho values are obtained depending on the method employed suggests that also an association of the hydrocarbon with the catalyst center, perhaps taking place in the transition state of the oxidation, may be envisaged. In fact, the larger

Table 3
Oxidation of variously substituted 0.6 M ethylbenzenes by 0.02 M Ph_4PHSO_5 catalyzed by 6.0×10^{-5} M Mn(TMP)Cl in the presence of 9.5×10^{-2} M 4-*tert*-butylpyridine, in DCE at 30°C

Entry	Substrate	$k_{obs.}$ (ketone) $\times 10^4$ (s^{-1})	[ketone]/[alcohol]
1	4-CH_3-ethylbenzene	5.0	2.8
2	ethylbenzene	4.0	5.4
3	4-Br-ethylbenzene	3.5	19.8
4	4-NO_2-ethylbenzene	2.5	∞

Table 4
Competitive oxidation of variously substituted 0.6 M ethylbenzenes by 0.02 M Ph_4PHSO_5 catalyzed by 6.0×10^{-5} M Mn(TMP)Cl in the presence of 9.5×10^{-2} M 4-*tert*-butylpyridine, in DCE at 30°C

Entry	Substrates	Products, yields (%)[a]	k_X / k_H^b
1	4-CH_3-ethylbenzene + ethylbenzene	4-CH_3-acetophenone , 43.6 1-(4-CH-$_3$-phenyl)ethanol, 11.7 acetophenone, 26.5 1-phenylethanol, 4.9	1.85
2	4-Br-ethylbenzene + ethylbenzene	4-Br-acetophenone , 35.4 1-(4-Br-phenyl)ethanol, 2.2 acetophenone, 38.7 1-phenylethanol, 5.8	0.79
3	4-NO_2-ethylbenzene + ethylbenzene	4-NO_2-acetophenone , 18.6 acetophenone, 49.1 1-phenylethanol, 6.2	0.30

[a] The yields are based on the oxidant according to the stoichiometry: 1 mol alcohol = 1 mol monoperoxysulfate and 1 mol ketone = 2 mol monoperoxysulfate.

[b] The ratios k_X / k_H are obtained by dividing the concentrations of ketone and alcohol originated from the X substituted ethylbenzene by the concentrations of ketone and alcohol originated from ethylbenzene.

selectivity observed in the competitive experiments compared to that found in individual experiments may be explained by assuming that the more electron-rich species competes with the other substrate, simultaneously present, for the association to the catalyst thus inhibiting its oxidation, as depicted in Scheme 4.

Furthermore, both rho values are small thus indicating a scarce charge separation in the transition state of the r.d.s. [21]. As a consequence, a mechanistic pathway involving either a heterolytic hydride or proton abstraction, appears rather unlikely [22]. On the other hand, a small charge separation in the transition state of the r.d.s. agrees with both a radical hydrogen abstraction or a concerted oxygen insertion into the aliphatic C–H bond. Therefore we studied the oxidation of hydrocarbons and alcohols in the presence of manganese porphyrinate catalysts and of cobalt or iron derivatives. The hydrocarbon/alcohol reactivity ratios observed when the oxo-manganese porphyrinate is the oxidant compared with the ratios measured in the Co or Fe-based oxidizing systems whose radical behavior is well established, could provide more information on the occurrence of hydrocarbon–manganese association as well as on the nature of the intimate mechanism of oxidation. In fact the results

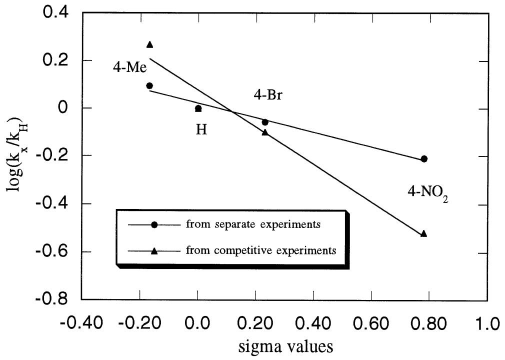
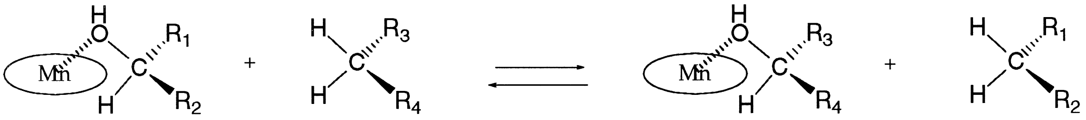


Fig. 3. Hammett plots for the oxidation of 0.6 M 4× substituted ethylbenzenes with 2.0×10^{-2} M Ph_4PHSO_5 catalyzed by 6.0×10^{-5} M Mn(TMP)Cl in the presence of 2.7×10^{-3} M 4-*tert*-butylpyridine in DCE at 30°C, determined by separate (●) and competitive (▲) experiments.



Scheme 4.

obtained by competitive experiments, in which any possible kinetic interference caused by steps preceding the formation of the effective oxidizing species is eliminated, allow to establish the intrinsic reactivity of such an oxidant toward the substrate. Owing to the difficulty of obtaining hydrocarbon/alcohol reactivity ratios in a simple competitive experiment because of the impossibility to discriminate between the ketone formed from the hydrocarbon and that formed from the alcohol, we decided to measure the reactivity ratios toward a third substrate, i.e. cumene, in two independent competitive experiments. In such a way it is possible to measure the hydrocarbon/alcohol reactivity ratios simply by dividing the two hydrocarbon/cumene alcohol/cumene reactivity ratios. In Table 5 the pertinent results are reported.

Both manganese porphyrins tested (entries 1 and 2) give very similar alcohol/hydrocarbon reactivities. These values differ from those determined in single experiments (Table 2). This is again likely the result of the association of the substrate to the oxo-manganese species. In addition they indicate a very similar reactivity toward the oxo-manganese–porphyrinate. This finding does not fit with a mechanistic scheme in which a hydrogen atom abstraction is taking place in the r.d.s. of the catalytic process. In fact, when such a mechanistic scheme is operating, large alcohol/hydrocarbon ratios are observed because of the remarkable stabilization of a carbon centered radical in α position to an oxygen atom [23]. Accordingly, the reactivity ratio for the radical oxidant $SO_4^{-\cdot}$, generated by Co(II) and Fe(II) derivatives (entries 5 and 6), is significantly in favor of the alcoholic substrate as expected. Moreover, the reactivity ratio observed for the system $Co(II)(acac)_2/HSO_5^-$ is similar to that found in individual experiments (Table 2), thus indicating that substrate–oxidant association in this case does not play a significant role. In a previous paper [4] we have shown that the substitution of the nitrogen base with an anionic oxygen base such as tetrabutyl ammonium benzoate in the reaction of a manganese porphyrin with Ph_4PHSO_5 is accompanied by the formation of a new Soret band at 421 nm, probably related to a manganese (IV) oxospecies. Such a new manganese derivative oxidizes olefins in a non stereospecific way as radical oxidants usually do [5,24]. Experiments 3 and 4 of Table 5 show that such a change in the nature of the axial ligand coordinated to the catalyst induces a remarkable enhancement of the oxo-manganese porphyrinate reactivity toward the alcohol. This result suggests that also in this case two different oxomanganese species are acting in the two systems. In particular, the much larger reactivity of the alcohol compared with that of the hydrocarbon

Table 5
1-phenylethanol versus ethylbenzene reactivity with 0.02 M Ph_4PHSO_5 measured by competitive experiments with cumene, in the presence of various catalysts, in DCE at 30°C

Entry	Catalyst	$k_{(1\text{-phenylethanol})}/k_{(\text{ethylbenzene})}$
1	Mn(TMP)Cl/4-*tert*-butylpy.	6.1
2	Mn(TDCPP)Cl/4-*tert*-butylpy.	2.2
3	Mn(TMP)Cl/benzoate	16
4	Mn(TDCPP)Cl/benzoate	53
5	$Co(acac)_2$	191
6	$Fe(acac)_2$	502

in the oxidation promoted by manganese porphyrin with benzoate as axial ligand indicates that for these compounds the corresponding oxo-species has a definite radical character. Accordingly hydrogen abstraction from a carbon atom in the α-position to an alcoholic group is easier than that from a simple hydrocarbon [25,26].

By contrast for the Mn(TMP)Cl/pyridine system both, the small charge separation in r.d.s. and the similar alcohol/hydrocarbon reactivity suggest a concerted oxo–oxygen insertion into the aliphatic C–H bond.

To conclude, in this paper the importance of alcohol coordination to the manganese porphyrin in determining the chemioselectivity of the oxidative process has been confirmed. Moreover, the evidence that hydrocarbon may coordinate to the oxo-manganese derivative has been obtained. The comparison of the reactivities toward ethylbenzene and 1-phenylethanol of various oxidizing systems employing Ph_4PHSO_5 as primary oxidant and Mn(TMP)Cl/pyridine, Mn(TMP)Cl/benzoate and $Co(II)(acac)_2$ as catalyst suggest that different mechanism for oxo-oxygen transfer to organic substrates are operating. In particular, Mn(TMP)Cl/benzoate catalyst shows a behavior compatible with the classic hydroxylation mechanism accepted for iron porphyrin while Mn(TMP)Cl/pyridine catalyst seems to transfer the oxo oxygen into a C–H bond through a concerted mechanism.

3. Experimental section

3.1. Materials

1,2-dichloroethane (DCE) was purified by distillation over P_2O_5. Spectrophotometric grade methanol (99.9%) and *tert*-butyl alcohol, a high purity product (> 99.5) from Aldrich company, were used without further purification. Ethylbenzene was purified by distillation over $NaBH_4$. Tetramesitylporphyrin ($TMPH_2$) and 2,6-dichlorophenylporphyrin ($TDCPPH_2$) were synthesized following a slightly modified Smith method [27,28]. The metallation of $TMPH_2$ and $TDCPPH_2$ with $Mn(II)(OAc)_2$ was performed by conventional methods [29,30]. Ph_4PHSO_5 was prepared and purified as previously reported [31]. Oxone, tetraphenylphosphonium chloride, cobalt and iron acetylacetonate, bromobenzene (GLC internal standard), 4-*tert*-butyl pyridine, 4-Me-ethylbenzene, 4-NO_2-ethylbenzene and 1-phenylethanol were all commercially available high purity products (Aldrich) used as received. The tetrabutylammonium salt of benzoate was prepared according to a previously reported procedure [4].

3.2. 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 and 3.0 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 analyzed by GLC analysis. Duplicate runs agreed within $\pm 5\%$ which can be considered the error of the rate constants.

3.3. Kinetic measurements: Competitive reactions

Competitive reactions were performed following the general procedure described in Section 3.2 with the exception that solution B contains 3.0 mmol of each substrate. The relative rate constant of substrate 2 with respect to substrate 1 was determined by dividing the sum of the concentrations of the ketone and alcohol formed from substrate 2 by the sum of the concentrations of the ketone and alcohol formed from substrate 1. For instance, the relative rate constant for ethylbenzene and 4-NO_2-ethylbenzene is obtained by the following equation:

$$\frac{k_{4-\mathrm{NO_2}-\mathrm{ethylbenzene}}}{k_{\mathrm{ethylbenzene}}}=\frac{[1-(4-\mathrm{NO_2}-\mathrm{phenyl})\mathrm{ethanol}]_{t=\infty}+[4-\mathrm{NO_2}-\mathrm{acetophenone}]_{t=\infty}}{[1-\mathrm{phenylethanol}]_{t=\infty}+[\mathrm{acetophenone}]_{t=\infty}}$$

For the alcohol/alkane reactivity evaluation (Table 5) two competitive experiments with cumene are needed. In the first the alcohol and cumene are pitted together to compete for the oxidant as above decribed. By means of this experiment the ratio $k_{\mathrm{alcohol}}/k_{\mathrm{cumene}}$ is obtained:

$$\frac{k_{\mathrm{alcohol}}}{k_{\mathrm{cumene}}}=\frac{[\mathrm{ketone}]_{t=\infty}}{[\mathrm{cumylalcohol}]_{t=\infty}}$$

In the second experiment the alkane is pitted together with cumene to compete for the oxidant and the ratio $k_{\mathrm{alkane}}/k_{\mathrm{cumene}}$ is obtained:

$$\frac{k_{\mathrm{alkane}}}{k_{\mathrm{cumene}}}=\frac{[\mathrm{alcohol}]_{t=\infty}+[\mathrm{ketone}]_{t=\infty}}{[\mathrm{cumylalcohol}]_{t=\infty}}$$

Finally the alcohol/alkane reactivity ratio is obtained by dividing $k_{\mathrm{alcohol}}/k_{\mathrm{cumene}}$ by $k_{\mathrm{alkane}}/k_{\mathrm{cumene}}$.

3.4. Simulation of kinetic profiles

The simulated curves for product appearance in alkane oxidation by Ph_4PHSO_5 catalyzed by Mn(TMP)Cl porphyrin were obtained by the kinetic simulation program HopKIMSIM, based on Barshop and Friden’s KINSIM for the VAX.

3.5. Instruments

The concentrations of the products in the oxidation of alkanes and alcohols were determined by GLC analysis with the internal standard method on the basis of previously calculated response factors. The analysis were performed on a Carbowax 20 M, 10% 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 gas chromatograph, 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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