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HYDROCARBON OXIDATION WITH Ph_4PHSO_5 CATALYZED BY MANGANESE(III) PORPHYRINS IN HOMOGENEOUS SOLUTION

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The oxidation of ethylbenzene with Ph_4PHSO_5 catalyzed by Mn(TMP)Cl in the presence of 4-*tert*-butylpyridine was studied in 1,2-dichloroethane. The reaction affords acetophenone together with minor amounts of 1-phenylethyl alcohol. The oxidation of 1-phenylethyl alcohol to acetophenone was studied under identical experimental conditions. In both cases, the oxidation rates are independent of the concentration of the substrates whereas they depend linearly on catalyst concentration. By increasing the concentration of 4-*tert*-butylpyridine, which acts as an axial ligand of the catalyst, saturation behavior is observed. The observations reported above, together with the chemoselectivity observed, the fact that the reactivities of the alkane and of the alcohol are similar and the activation parameters of ethylbenzene oxidation ($\Delta H^{\ddagger} = 57$ kJ mol^{-1}, $\Delta S^{\ddagger} = -134$ J K^{-1} mol^{-1}) are rationalized on the basis of the formation of an alkane–oxo-porphyrinato complex. The ketone is generated by further oxidation of the alcohol, produced from the intermediate, still present in the coordination sphere of the metal. Furthermore, it is suggested that the hydroxylation proceeds through a concerted insertion of the oxo-oxygen on the hydrogen–carbon bond rather than through a recombination of radicals. The formation of the ketone appears to be better accommodated in a reaction scheme in which the product is formed via an oxygenation of the alcohol to give a geminal diol rather than through dehydrogenation.

INTRODUCTION

The selective hydroxylation of saturated hydrocarbons remains a delicate transformation since alcohols are usually more oxidizable than the parent hydrocarbons.[1] The observation that in living organisms metalloenzymes such as methane monooxygenase or cytocrome P-450 selectively catalyze the hydroxylation of various substrates[2] indicated that metalloporphyrin catalysts in association with an appropriate oxygen donor may be selective oxidizing systems. In fact, such chemical systems have been shown to mimic several oxidative transformations carried out by the enzymes of the cytochrome P-450 family.[3] The origin of the selectivity of enzymes and enzyme-like systems, i.e. the intimate mechanism of hydrocarbon hydroxylation, is still a matter of debate.[4] A kinetic investigation of catalytic oxidation may be a powerful tool in elucidating their reaction mechanisms, provided that the appropriate experimental conditions are used. This requirement is not easily fulfilled in metalloporphyrin oxidation chemistry. As an example, in many cases two-phase systems need to be used. Whereas the organic substrate and the catalyst are usually soluble in organic solvents, the commonly used oxygen donors are soluble only in water.[5] As a result, these systems may be complicated by the occurrence of several processes other than the oxidation reaction.

In previous papers, we reported on the general features of the oxidizing system employing tetraphenylphosphonium monoperoxosulfate, Ph_4PHSO_5, as oxygen donor and manganese(III) porphyrins in association with an axial ligand (neutral or anionic bases) as catalysts.[6–8] This system is particularly suitable for mechanistic studies which may be carried out under homogeneous conditions owing to the solubility of the peroxide in non-polar solvents such as 1,2-dichloroethane (DCE). In addition, the negligible reactivity of the monoperoxosulfate towards organic substrates allows the contribution of the uncatalyzed oxidation to be neglected.[7,8]

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The following are examples of useful information obtained by kinetic studies under homogeneous conditions. It has been found that the presence of species capable of acting as axial ligands of the catalyst, e.g. neutral nitrogen bases, is a prerequisite for the formation of an oxo-manganese species (oxene) which is the real oxidant.[6] It has also been observed that the mono- and bis-adducts, resulting from the complexation of one or two molecules of the ligand with the manganese porphyrin, form the oxene at almost the same rate,[6] at variance with the behavior of two-phase systems in which the mono-adduct is more reactive than the bis-adduct.[9] Weak anionic bases, e.g. ClO_4^-, SO_4^{2-} and CH_3COO^-, can also act as axial ligands of manganese porphyrins and promote the formation of an oxo species.[7] Both the nature and the reactivity of oxo species depend on the nature of the axial ligand, i.e. neutral nitrogen vs anionic oxygen bases, as shown by the difference in spectroscopic properties and by the different selectivities in alkene oxidation.[7]

In spite of the peculiarities of the homogeneous system described above, the general outcome of the oxidation of organic substrates carried out in such a system is similar to that established for the more traditional two-phase systems. As an example, the chemo- and stereoselectivity of alkene epoxidation are the same.[5] There is, however, at least one exception revealed by preliminary experiments. We found that the chemoselectivity of the oxidation of the aliphatic C – H bond is different in the two oxidizing procedures. In particular, whereas alkane oxidation in two-phase systems yields a mixture of alcohols and ketones in variable ratios,[5] in our homogeneous system the formation of ketones is the favored reaction so that only minor amounts of alcohols are obtained. This result could indicate that a peroxidase-like reactivity prevails over the oxygenase-like reactivity[10] triggered by the change of the conditions. We therefore decided to investigate the oxidation of the C—H aliphatic bond in our system in more detail. In this paper, we confirm that the corresponding ketone is by far the major product of the oxidation of ethylbenzene and other hydrocarbons. Our results suggest also a non-radical nature of the oxidation. Moreover, it appears that the ketone is formed via two subsequent oxygen transfers, leading to a geminal diol rather than via one oxygen transfer followed by a dehydrogenation process of the alcohol formed.

RESULTS AND DISCUSSION

The oxidation of ethylbenzene with Ph_4PHSO_5 catalyzed by Mn(TMP)Cl in the presence of 4-*tert*-butylpyridine in the ratio 10000:300:1:300 in DCE proceeds smoothly at room temperature. We measured the yields of the two products, acetophenone and 1-phenylethyl alcohol. These yields, based on the primary oxidant consumed, range from 40 to 100% depending on the temperature and on the substrate and axial ligand concentrations. In particular, an almost 100% yield is obtained by using a 33-fold excess of substrate over the oxidant and a 1600-fold excess of ligand over the catalyst at 0 °C. At lower excesses, lower yields are obtained, thus indicating that processes involving oxidant self-decomposition are also operating.[11] The yields increase with increasing axial ligand concentrations up to a maximum. At higher 4-*tert*-butylpyridine concentrations a decrease in the yields is observed. This behavior is probably due to the concomitant nitrogen base oxidation, already observed in previous studies.[5]

The gas–liquid chromatographic (GLC) analysis of the reaction mixtures revealed that the main product is acetophenone (75–95%) whereas 1-phenylethylalcohol is present only in minor amounts (5–25%). The oxidation rates were measured by determining, at the appropriate time intervals, the concentration of acetophenone by GLC analysis. The corresponding rate constants were obtained from integrated pseudo-first-order plots, i.e. $(1/2)\ln([\text{ketone}]_\infty - [\text{ketone}]_t)$ vs time (t), which were linear up to 50% reaction, thus indicating that the kinetic order in oxidant is one. Figure 1 shows the behavior of the appearance of the products as a function of time in a typical oxidation reaction.

Although the simplest pathway that one may envisage for acetophenone formation is by further oxidation of 1-phenylethyl alcohol, this appears not to be the case here. In fact, one would expect an increase in 1-phenylethylalcohol at the beginning of the reaction followed by a decrease due to the consecutive oxidation to ketone. This would result in a bell-shaped kinetic profile. Moreover, the formation of ketone should exibit an

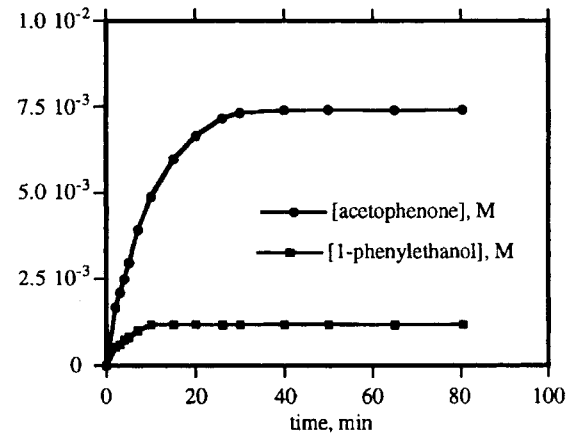


Figure 1. Appearance of the products as a function of time in the oxidation of 0·6 M ethylbenzene with $2{\cdot}0\times10^{-2}$ M Ph_4PHSO_5 catalyzed by $6{\cdot}0\times10^{-5}$ M Mn(TMP)Cl in the presence of $2{\cdot}7\times10^{-3}$ M 4-*tert*-butylpyridine in DCE at 30 °C

induction period corresponding to the initial formation of the alcohol. Figure 1 shows that the experimental outcome is completely different from the prediction. Rather, it appears that two parallel processes are occurring. The possibility that the behavior in Figure 1 is due to a large difference in the specific rate constants of the two consecutive processes, i.e. that the oxidation of the alkane to alcohol is much slower than the oxidation of the alcohol to ketone, should be considered unlikely. In fact, the rate of formation of the alcohol should not be much larger than that of the ketone because of the large excess of alkane employed. In addition, as will be discussed later, we directly checked that the alcohol-forming reaction is only twofold slower than the ketone-forming reaction. In Table 1 are shown the results obtained by varying the concentration of alkane, catalyst, axial ligand and oxidant at constant concentrations of all the other species.

Runs 1–8 in Table 1 show that the kinetic order of the alkane is zero at both temperatures examined, 0 and 30 °C. It may be mentioned that in the oxidation of cyclooctene, which is more reactive than ethylbenzene under the same conditions as in runs 1–4, a kinetic order of one in alkene is observed at substrate concentrations below 5×10^{-2} M.[8] The order tended to zero when the substrate concentration was increased above 0·1 M.[8]

In the case of alkene epoxidation, the rationale is that at the highest alkene concentrations the rate-determining step (r.d.s.) of the reaction becomes oxene formation. If this were the case here, in the oxidation of the less reactive ethylbenzene, one would expect that the rates of oxidation would become independent of substrate concentrations only at very high alkane excesses (≥0·1 M). On the contrary, the rates of ethylbenzene oxidation are almost independent of substrate concentration even at the lowest concentrations employed. This suggests that alkane oxidation must be accommodated in a different mechanistic scheme than that proposed for alkene oxidations. In particular, the zero order of the substrate suggests the equilibrium formation of an intermediate resulting from the alkane–oxene interaction whose concentration corresponds to the concentration of the oxene because of the large excess of the hydrocarbon which shifts the equilibrium to the right.

Runs 1–4 and 5–8 in Table 1 provide further mechanistic information by indicating that the ketone to alcohol ratio decreases by a factor of three when ethylbenzene is increased by a factor of ten. This again does not fit with the hypothesis of two simple consecutive reactions. Runs 13–19 show that on increasing the concentration of 4-*tert*-butylpyridine the amount of alcohol increases. This provides mechanistic clues which will be discussed later. Runs 7, 11 and 12 in Table 1 establish that the kinetic order of the catalyst is one. Runs 7, 9 and 10, showing that the pseudo-first-order rate constants do not depend on the initial concen-

Table 1. Effect of temperature and of substrate, catalyst, ligand and oxidant concentrations on the pseudo-first-order rate constants of ethylbenzene oxidation[a]

Run No.	Temperature (°C)	[Ethylbenzene] (M)	[Mn(TMP)Cl] (10^{-5} M)	[4-*tert*-Butyl-pyridine] (10^{-2} M)	[Ph_4PHSO_5] (10^{-2} M)	$k_1 \times 10^4$ (s^{-1})[b]	[Ketone]/[alcohol]
1	0	0·16	6·0	9·5	2·0	0·49	6
2	0	0·33	6·0	9·5	2·0	0·51	5
3	0	0·65	6·0	9·5	2·0	0·58	4
4	0	1·3	6·0	9·5	2·0	0·73	2·5
5	30	0·16	6·0	9·5	2·0	6·5	16
6	30	0·33	6·0	9·5	2·0	6·3	11
7	30	0·65	6·0	9·5	2·0	6·3	6
8	30	1·3	6·0	9·5	2·0	6·6	5
9	30	0·65	6·0	9·5	3·4	6·3	8
10	30	0·65	6·0	9·5	1·0	6·2	3
11	30	0·65	3·0	9·5	2·0	3·3	4
12	30	0·65	12·1	9·5	2·0	13·1	4
13	30	0·65	6·0	0·27	2·0	1·2	16
14	30	0·65	6·0	0·54	2·0	1·7	12
15	30	0·65	6·0	0·68	2·0	2·0	18
16	30	0·65	6·0	1·4	2·0	2·6	11
17	30	0·65	6·0	2·7	2·0	4·6	8
18	30	0·65	6·0	5·4	2·0	5·9	7
19	30	0·65	6·0	13·5	2·0	6·7	4

[a] The reactions were carried out in 1,2-dichloroethane.
[b] The rate constants refer to acetophenone formation.

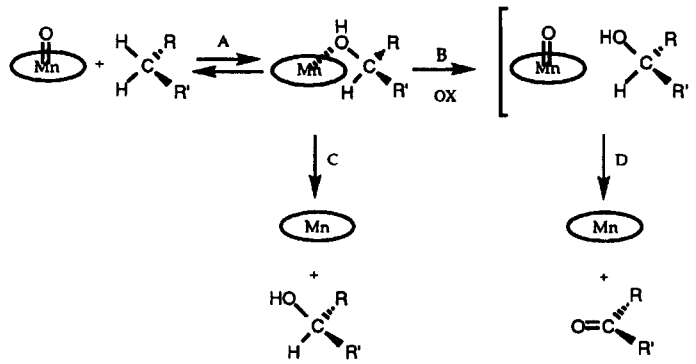
tration of Ph_4PHSO_5, confirm that the kinetic order of the oxidant is one. In addition, they show that the [ketone] to [alcohol] ratio increases with increasing oxidant concentration.

All these observations can be interpreted by assuming that the alcohol formed from the alkane–oxene intermediate remains coordinated to the porphyrin complex undergoing a second oxidation to ketone. This hypothesis is shown in Scheme 1, which at this stage, must be considered a very simplified picture of the process. In this mechanistic picture, the small amount of alcohol found in the reaction mixture comes from path C. Such alcohol, free in solution, does not undergo further oxidation, probably because of the very large excess of the competing alkane.

According to Scheme 1, the alcohol to ketone ratio is determined by the relative rates of paths C and D and therefore an increase in the alkane concentration should not affect such a ratio, provided that step B, i.e. the oxygen transfer to the metalloporphyrin, is fast in comparison with steps C and D. Scheme 1 also provides a rationale for the dependence of the ketone to alcohol ratio on Ph_4PHSO_5 concentration. In fact, on increasing the initial concentration of oxidant, step B and consequently step D become faster than step C, thus favoring ketone formation. It may be noted that Scheme 1 takes into account the rationale of the zero-order dependence of rates on alkane concentration. As already discussed, under the hypothesis of the equilibrium formation of a substrate–oxene intermediate, the limiting concentration is that of the oxo species formed in step B. It may also be observed that an increase of the axial ligand concentration should affect the rate of path C, since the nucleophilic species may replace the coordinated alcohol. This explains the change in selectivity with increasing axial ligand concentration. Experiments 13–19 in Table 1 show that the oxidation rates reach a plateau at high axial ligand to catalyst ratios, thus confirming that also in alkane oxidation mono- and bis-adducts of metalloporphyrin–axial ligands are formed and that their ability to form the oxene is similar.[6] The activation parameters for acetophenone formation ($\Delta H^{\ddagger} = 57$ kJ mol^{-1}, $\Delta S^{\ddagger} = -134$ J K^{-1} mol^{-1} measured in the range 0–30 °C) and in particular the large negative entropy of activation are typical of bimolecular reactions.

It should be mentioned that the results presented so far do not allow one to discriminate between a concerted insertion of the oxo-oxygen into the C – H bond[12] of the substrate and the formation of a radical pair[12,13] which collapses to products. Also the hypothesis that only the alcohol coordinated to the metal undergoes oxidation, whereas the alcohol free in solution does not, needs to be corroborated. In order to address these aspects, we investigated the oxidation of 1-phenylethyl alcohol to acetophenone under the same experimental conditions as adopted for the ethylbenzene oxidation. Table 2 gives the pertinent results.

The kinetic picture for alcohol oxidation is very similar to that found for alkane oxidation. In fact, experiments 1–4 in Table 2 indicate no dependence of the reaction rates on substrate concentration. Moreover, experiments 5–9 show a less-than-one kinetic order of axial ligand, suggesting that saturation of the catalyst by the nitrogen base is also taking place here. Experiments 10–12 allow one to calculate a kinetic order of the catalyst very close to unity. The reactivity of 1-phenylethyl alcohol is only about twice that of ethylbenzene. This militates against the possibility that the alcohol is a reaction intermediate in a simple system of two consecutive oxidations. Moreover, such a similar reactivity does not fit a mechanism involving hydrogen radical abstraction followed by a fast recombination of the two radicals leading to the products.[13] In fact, if this were the case, one would expect that the alcohol would be much more reactive than the alkane, in line with the fact that hydrogen radical abstraction is much easier from the α-carbon of an alcohol than from an alkane.[14] Hence the results obtained are better interpreted by suggesting that the hydroxylation process proceeds through an



Scheme 1

Table 2. Effect of substrate, catalyst, ligand and oxidant concentrations on the pseudo-first-order rate constants of 1-phenylethyl alcohol oxidation[a]

Run No.	[1-Phenylethyl alcohol] (M)	[4-*tert*-Butyl-pyridine] (10^{-2} M)	[Mn(TMP)Cl] (10^{-5} M)	$k_1 \times 10^{-3}$ (s^{-1})	Acetophenone yield (%)
1	0·165	9·5	6·0	1·35	71
2	0·33	9·5	6·0	1·34	65
3	0·66	9·5	6·0	1·31	67
4	1·32	9·5	6·0	1·28	69
5	0·66	0·14	6·0	0·25	62
6	0·66	0·68	6·0	0·69	70
7	0·66	1·4	6·0	0·77	73
8	0·66	2·7	6·0	0·79	76
9	0·66	5·4	6·0	0·93	80
10	0·66	2·0	3·1	0·44	68
11	0·66	2·0	6·2	1·04	81
12	0·66	2·0	12·4	2·1	76

[a] The reactions were carried out in 1,2-dichloroethane at 30 °C.

oxene insertion into the C – H bond either of the alkane or of the alcohol. A corollary of this proposal is that the ketone also is generated through an oxygenation process rather than through an alcohol dehydrogenation. The value of the kinetic isotope effect obtained in the oxidation of ethylbenzene and ethylbenzene-d_{10}, i.e. 2·7 (see Table 3), indicates that the cleavage of the carbon–hydrogen bond leading to acetophenone occurs in a slow step. The comparison of the relative reactivities of ethylbenzene, diphenylmethane and fluorene provides further mechanistic information. The data for such a comparison are given in Table 3.

For the first two substrates (runs 2 and 3), the reactivity order is not in agreement with the order of the stability of the corresponding radicals, which is diphenylmethyl > methylbenzyl.[15] At any rate, it may be observed that the values of the rate constants span a very narrow interval, suggesting that the formation of an alkyl radical does not play a key role in the oxidative process. In the case of fluorene, the only product obtained, in low yield, is 9-hydroxyfluorene. It may also be noted that the rate of alcohol formation from fluorene is considerably larger than that of ketone formation from the other two substrates. This might indicate that, owing to the high lability of the hydrogen of fluorene, this is the case in which a radical hydrogen abstraction takes place. This also fits with the low yield (12%) obtained, since it is likely that an induced radical decomposition of the oxidant occurs. The second oxygenation to give 9-fluorenone is probably prevented by steric factors, since the geometry of the α-hydroxyfluorene hinders its coordination to the manganese porphyrin.

We may now summarize the relevant information provided by the data presented in this paper. It has been shown that the chemoselectivity of alkane oxidation with Ph_4PHSO_5 catalyzed by Mn(TMP)Cl is determined by the experimental conditions adopted and in particular by the reaction medium. Low-polarity solvents, such as dichloroethane, and low concentrations of species able to act as axial ligands of the catalyst favor ketone formation because they favor the coordination of the alcohol to the metal. Furthermore, the mechanism of the hydroxylation reaction appears to be affected by the

Table 3. Effect of hydrocarbon structure on reaction rates and products distribution in alkane oxidation[a]

Run No.	Substrate	$k_{ketone} \times 10^4$ (s^{-1})	$k_{alcohol} \times 10^4$ (s^{-1})	Yield (%)	[Ketone]/[alcohol]
1	Ethylbenzene-d_{10}	2·3	-	14[b]	6
2	Ethylbenzene	6·3	-	55[b]	6
3	Diphenylmethane	4·2	-	52[c]	11
4	Fluorene	-	18	12[d]	0

[a] The reactions were carried out in the presence of 0·65 M substrate, $2·0 \times 10^{-2}$ M Ph_4PHSO_5, $6·0 \times 10^{-5}$ M Mn(TMP)Cl and $9·5 \times 10^{-2}$ M 4-*tert*-butylpyridine in dichloroethane at 30 °C.
[b] [1-Phenylethyl alcohol] + [acetophenone].
[c] [Diphenylcarbinol] + [benzophenone].
[d] [9-Hydroxyfluorene].

nature of the substrate. In particular, in the case of alkanes, whose radicals exibit moderate stability, such as ethylbenzene and diphenylmethane, oxygen insertion into the C – H bond probably takes place via a polar rather than a radical mechanism. In contrast, when the substrate may lead to a very stable radical, such as in fluorene oxidation, the hydroxylation proceeds through a radical mechanism. Finally, the alcohol oxidation to ketone follows the same rate law as that of the corresponding alkane, suggesting that ketone is formed via two subsequent oxo-oxygen insertions, giving a geminal diol which then evolves to ketone.

EXPERIMENTAL

Materials. 1,2-Dichloroethane (DCE) was purified by distillation over P_2O_5. Tetramesitylporphyrin ($TMPH_2$) was synthesized following a slightly modified Lindsay Smith method.[16] The metallation of $TMPH_2$ with $Mn^{II}(OAc)_2$ was performed by conventional methods.[17] Ph_4PHSO_5 was prepared and purified as previously reported.[6] Ethylbenzene was purified by distillation over $NaBH_4$. 9-Hydroxyfluorene was purified by cristallization from ethanol. Peroxomonosulfate triple salt (oxone), tetraphenylphosphonium chloride, 1-phenylethanol, fluorene, bromobenzene (GLC internal standard when ethylbenzene or 1-phenylethanol was the substrate) and benzophenone (GLC internal standard when fluorene or 9-hydroxyfluorene was the substrate) were all commercially available, high-purity products (Aldrich) and were used as received.

Kinetic measurements. Typically, the reactions were initiated by adding 2 ml of a DCE solution containing 0·10 mmol of Ph_4PHSO_5 to 3 ml of DCE solution containing $3{\cdot}1 \times 10^{-4}$ mmol of Mn(TMP)Cl, 4×10^{-2} mmol of internal standard and 3·0 mmol of substrate, in a jacketed reactor thermostated at 30 °C. At appropriate time intervals, 0·10 ml portions of reaction mixture were withdrawn, quenched with an equivalent volume of 0·4 M PPh_3 solution in DCE and analysed by GLC. Duplicate runs agreed to within ±5%, which can be considered the error in the rate constants.

Instruments. Product concentrations in alkane oxidation were determined by GLC on the basis of previously calculated response factors toward an appropriate internal standard on a 10% Carbowax 20M on Chromosorb WAW–DMCS (80–100 mesh) column (1·8 m). The gas chromatograph was a Varian Model 3700 equipped with a Shimadzu C-R3 A data processor.

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