

Formation and reactivity toward hydrocarbons of oxomanganese porphyrins in the presence of anionic bases

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Abstract

In dichloroethane oxygen transfer from Ph_4PHSO_5 to manganese(III) porphyrins forming the corresponding oxo-species, which then oxidize organic substrates, occurs only in the presence of basic species acting as axial ligands. Together with neutral nitrogen bases such as pyridines and imidazole, anionic bases, i.e., ClO^- , SO_3^{2-} , and CH_3CO_2^- , promote the formation of oxo-manganese porphyrin species. However, on the basis of a comparison of the spectral properties and of the oxidative behaviors towards *cis*-stilbene and diphenylmethane, we suggest that the oxo-species formed in the presence of anionic oxygen bases is different from that formed in the presence of neutral bases. In particular, the former is suggested to be a manganese(IV) derivative behaving as a radical oxidant.

Keywords: Alkenes; Anionic bases; Epoxidation; Hydrocarbons; Oxidation; Manganese; Porphyrins; Tetraphenylphosphonium peroxomonosulfate

1. Introduction

Recently some general features of the oxidizing system based on Ph_4PHSO_5 (tetraphenylphosphonium peroxomonosulfate) as oxygen donor and manganese(III) porphyrins (in the presence of nitrogen bases) as catalysts have been reported [1]. This system is particularly suitable for mechanistic studies owing to its simplicity. The peroxide, which can be prepared with a high degree of purity, is soluble in dichloroethane so that oxidation reactions can be carried out under homogeneous conditions. The rates of oxygen transfer from Ph_4PHSO_5 to the manganese porphyrins

leading to the oxo-manganese species have been measured by the stopped-flow technique in the absence of any oxidizable substrate (i.e., an alkene), and a second order rate law for this process has been established. In the presence of cyclooctene, quantitative yields of cyclooctene oxide are obtained. It is noteworthy that neither the formation of the oxo-manganese porphyrin species nor the epoxidation of the substrate occur in the absence of a nitrogen base capable of acting as axial ligand of the porphyrin complex. The presence of such bases, although essential, does represent a drawback of the oxidizing system. In fact, particularly when high concentrations of base are required, their competitive oxidation occurs. Thus the study of the effect of ligands which may

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play the same role as nitrogen bases while being, at the same time, resistant to oxidation is worthy of attention.

In this paper, we present results concerning the behavior of anionic oxygen bases, namely acetate, sulfate and perchlorate, in promoting the formation of an oxo species from Mn(TMP)Cl (5,10,15,20-tetramesityl manganese porphyrin) by Ph₄P₅SO₅. Hence substrate oxidation proceeds under the experimental conditions described above. On the basis of comparison of the spectroscopic properties and the chemical behavior in alkene and alkane oxidations by these oxo-derivatives with those properties of the oxo-intermediate obtained when imidazole is the axial base, we find that the two oxo-species behave differently. In particular, it is suggested that in the case of the anionic bases, the oxo-species should be described as a Mn(IV)-oxo-derivative exhibiting marked character as a radical oxidant [2,3].

2. Experimental section

Materials: 1,2-dichloroethane (DCE) and dichloromethane were purified by distillation over P₂O₅. Tetramesitylporphyrin (TMPH₂) was synthesized following a slightly-modified Lindsay Smith method [4]. The metallation of TMPH₂ was performed by conventional methods [5]. Ph₄P₅SO₅ was prepared and purified as previously reported [1]. Tetrabutylammonium salts of acetate, sulfate and perchlorate (Bu₄N⁺CH₃CO₂⁻, (Bu₄N⁺)₂SO₄²⁻, and Bu₄N⁺ClO₄⁻) were prepared by mixing the appropriate acid with a stoichiometric amount of tetrabutylammonium hydroxide (1.5 M solution in water). The solvent was then removed by distillation under vacuum. The remaining material was dissolved in CH₂Cl₂ and dried over MgSO₄. After removal of the MgSO₄ and solvent, the salt was obtained. Imidazole was purified by recrystallization from ethanol, and cobalt(II) acetate from THF. Peroxomonosulfate triple salt (oxone) tetraphenyl phosphonium chloride, *cis*-stilbene, diphenylmethane, acetic acid, perchloric acid, sul-

furic acid, and 1,2-dibromobenzene were all commercially available, high purity products (Aldrich or Janssen), used as received.

Procedures: Rate measurements of the oxo-species formation: in a typical run, a 2.5×10^{-2} M solution of Ph₄P₅SO₅ in DCE and a 1.25×10^{-5} M solution of Mn(TMP)Cl and 4.0×10^{-4} M of axial ligand in DCE were placed in the two compartments of a UV-visible cell and thermostated at the desired temperature. The reaction, initiated by mixing the two solutions, was monitored by recording the adsorption at the two wavelengths corresponding to the Soret band of the starting material (475 nm) and of the product (either 421 nm or 410 nm, see below). Duplicate runs agreed within 6%.

Product determinations in hydrocarbon oxidations: in a typical run 3 mL of DCE containing 1.92 mmol of diphenylmethane or *cis*-stilbene and 0.16 mmol of 1,2-dibromobenzene (internal standard) were added to a DCE (5 mL) solution containing the catalyst (5.0×10^{-4} mmol), the axial ligand (4.8×10^{-2} mmol) and the oxidant (0.16 mmol) in a glass reactor maintained at the appropriate temperature. After the consumption of the oxidant (checked by iodometric titration), the amounts of products were determined by GC analysis (on the basis of previously calculated response factors) on a Carbowax 20 M 10% (1.8 m column) WAW-DMCS.

Spectroscopic measurements: UV-visible spectra were recorded every 40 seconds after adding Ph₄P₅SO₅ to a solution of Mn(TMP)Cl and anionic base in a Perkin-Elmer Lambda 5 spectrophotometer.

3. Results and discussion

As previously reported [1] even when large excesses (up to 1000-fold) of Ph₄P₅SO₅ are added to a 1.0×10^{-5} M solution of Mn(TMP)Cl in DCE in the absence of any other additive, no reaction takes place as indicated by the invariance of the electronic spectrum of the manganese porphyrin. By adding relatively small amounts of

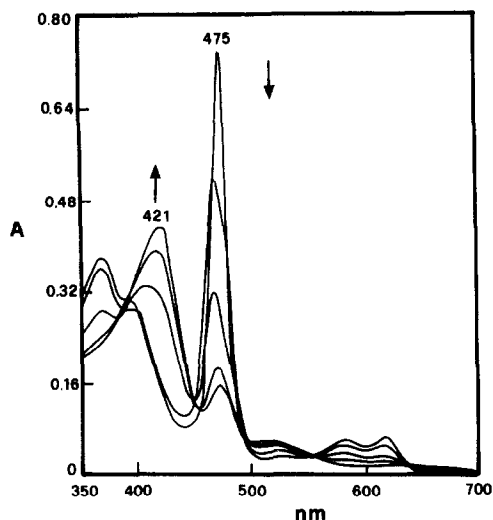
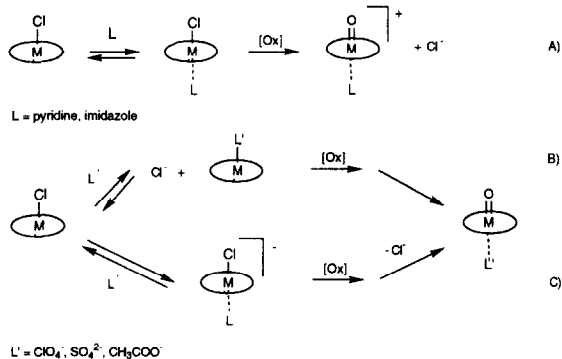


Fig. 1. Spectral changes observed during the reaction of 1×10^{-5} M Mn(TMP)Cl with 1.5×10^{-3} M Ph₄PHSO₅ in the presence of 4×10^{-4} M CH₃CO₂(Bu₄N) in DCE at 25°C. The time interval between each spectrum is 40 s.



(Bu₄N)CH₃CO₂, e.g. 1.0×10^{-4} M, the disappearance of the Soret band of Mn(TMP)Cl at 475 nm and the appearance of a new band at 421 nm are observed as shown in Fig. 1.

The assignment of this new band to an oxo-manganese species is based on the observation that it disappears in the presence of an oxidizable substrate. The corresponding oxidized products are obtained (see below). In one experiment, immediately after the formation of the band at 421 nm, an excess of cyclooctene was added and the band at 475 nm was completely restored. The GC analysis of the reaction mixture revealed that a fair yield of cyclooctene oxide, based on the amount of Ph₄PHSO₅, was obtained.

It should be noted that λ_{\max} (421 nm) for the oxo-species, which is the same for the three oxygen anions (CH₃CO₂⁻, SO₄²⁻ and ClO₄⁻) is red-shifted relative to that for the neutral nitrogen ligand, which is found at 410 nm. A number of factors may contribute to this difference: the atom binding to manganese in the oxo-species is not the same; the charge on the ligand differs and this may result in a change of charge on the oxo-complex; the number of unpaired electrons in the d orbitals of oxidized manganese may be different; and one electron may have been transferred from the π system of the porphyrin ring. A set of rather formal molecular differences can be sketched out to explain the red shift; some of these are given in Scheme 1, showing the formation of the oxo-species for which we favor the path B not only on the basis of the analogy with the neutral nitrogen ligands but also because direct experiments demonstrate that Mn(TMP)CH₃CO₂, prepared separately, is not oxidized by Ph₄PHSO₅ in the absence of (Bu₄N)CH₃CO₂.

The three oxygen anions all allow the rate of formation of the oxo-species to be measured by spectral measurements at 421 nm and the rate of loss of Mn(TMP)Cl at 475 nm. Some results are given in Table 1, and there is general agreement of the two rates. Also the rates are proportional to the ligand concentration. One imidazole run is

Table 1

Values of k_{obs} (s⁻¹) for the oxidation of 1.0×10^{-5} M Mn(TMP)Cl by 1.3×10^{-2} M Ph₄PHSO₅, in the presence of various bases, in DCE at 25°C

Entry	Base, M $\times 10^4$	$k_{\text{obs}}(478 \text{ nm}) \times 10^2$, s ⁻¹	$k_{\text{obs}}(421 \text{ nm}) \times 10^2$, s ⁻¹
1	–	n.r.	n.r.
2	CH ₃ COO ⁻ , 1.0	0.6	0.8
3	CH ₃ COO ⁻ , 2.0	0.9	1.3
4	CH ₃ COO ⁻ , 4.0	2.7	3.5
5	SO ₄ ²⁻ , 1.0	0.5	0.7
6	SO ₄ ²⁻ , 2.0	1.2	1.5
7	SO ₄ ²⁻ , 4.0	2.2	2.6
8	ClO ₄ ⁻ , 4.0	0.4	0.4
9	ClO ₄ ⁻ , 8.0	0.6	0.7
10	ClO ₄ ⁻ , 10.0	0.8	0.9
11 ^a	imidazole, 7.0	19.8	19.7

^a At 15°C.

given for comparison. The rate results confirm a previous conclusion that, if an intermediate is formed in the oxygen transfer process from Ph_4PHSO_5 to the manganese porphyrin, its concentration should be rather low. In the range of concentration explored, the kinetic order of the bases is one even though some ion aggregation effects might have been expected. It should also be noted that linear plots of k_{obs} versus base concentration are evidence of a rather small association of the oxygen bases to the metal so that a saturation behavior is not observed.

From the data of Table 1, the following order of increasing efficiency in forming the oxo-species is obtained for the bases examined: imidazole \gg acetate $>$ sulfate $>$ perchlorate. The same order is found for the $\text{p}K_{\text{a}}$ values of the conjugate acids of the bases even though they span a much larger interval (i.e. from 6.9 to -11) [6]. Even by allowing for the levelling effect of the solvent, the rather small differences found for the rate constants of Table 1 might indicate that the coordinating ability of the base is not the only factor playing a role.

The oxidative behaviors of the oxo-manganese porphyrin species promoted by two different bases plus peroxide catalysis separately are delineated in Table 2. Along with acetate ion and imidazole as porphyrin promoters oxidation data for cobalt(II) acetylacetonate with Ph_4PHSO_5 (in the absence of porphyrin) are presented. For the imidazole promoted system, a heterolytic oxidation is expected, at least for olefin epoxidation. On the other hand, the mixture of cobalt(II) and HSO_5^- forms one-electron oxidizing intermediates Co(III) and SO_4^- [7,8] so homolytic oxidation should occur.

The results for *cis*-stilbene oxidation are clear. For imidazole promotion a very high yield of the *cis*-epoxide, the stereospecific product, is obtained. By way of contrast, when cobalt(II) is the peroxide promoter, three products are obtained in good yield with a higher amount of the *trans*-epoxide which is rearranged product as compared to *cis*-epoxide. Considerable carbon-carbon cleavage also occurs in the cobalt system, as indi-

Table 2

Oxidation of two 0.24 M hydrocarbons by 0.02 M Ph_4PHSO_5 catalyzed by 6.3×10^{-5} M Mn(TMP)Cl in the presence of different additives, in DCE, at 30°C

Entry	Substrate	Additive, $\text{M} \times 10^3$	Yield, % ^a	Product distribution
1	<i>cis</i> -stilbene	–	0	–
2	<i>cis</i> -stilbene	imidazole, 6.0	63	<i>cis</i> -epoxide 96% <i>trans</i> -epoxide <4% PhCHO <1%
3 ^b	<i>cis</i> -stilbene	Co(acac)_2 , 1.0	35	<i>cis</i> -epoxide 14% <i>trans</i> -epoxide 50% PhCHO 36%
4	<i>cis</i> -stilbene	acetate, 6.0	60	<i>cis</i> -epoxide 22% <i>trans</i> -epoxide 35% PhCHO 44%
5	diphenylmethane	–	0	–
6	diphenylmethane	imidazole, 6.0	30	alcohol 20% ketone 80%
7 ^b	diphenylmethane	Co(acac)_2 , 1.0	60	alcohol 26% ketone 74%
8	diphenylmethane	acetate, 6.0	50	alcohol <1% ketone >99%

^a Yields calculated on the basis of active oxygen employed and measured when all the oxidant is consumed.

^b In the absence of Mn(TMP)Cl .

cated by 44% benzaldehyde. The results with acetate promoted manganese porphyrin strongly suggest that the oxidation occurred by a homolytic process.

The oxidation of diphenylmethane did not provide comparable unambiguous results as far as a mechanistic distinction between the three promoters is concerned. At any rate, a substantial homolytic character of the oxidation is suggested

in all cases. The amount of ketone was greater than the amount of alcohol even though oxidation was incomplete insofar as yields were concerned. It appears that alcohol is oxidized more rapidly than hydrocarbon irrespective of mechanism type.

The oxidation results do indicate that the acetate promoted system involves one-electron oxidation of the substrate as do also the cobalt(II) results. Nevertheless there are differences that reflect mechanistic complications, e.g., formation of cobalt(III) in the radical mechanism involved.

The red shift mentioned above may be related to the possibility that the anion promoted oxo-species have significant Mn(IV) character. This is substantiated by the observed radical character of the substrate oxidation. Literature data [9–14] confirms that the electronic spectra of Mn(IV) oxo-porphyrins are red-shifted relative to those of Mn(V) ones and that the former behave as radicals oxidants. Clearly a better understanding of the role of the axial ligands in determining electronic spectra and reactivities of the oxo-manganese species is needed. To this aim, further work is now in progress in our laboratory.

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