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Porphyrins and Azaporphines as Catalysts in Alkene Epoxidations with Peracetic Acid.

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Abstract: the reactivities of five Mn^{III}(Cl) - porphinoids were compared in the catalytic alkene epoxidations in CH₃CN solution with peracetic acid as primary oxidant. Porphyrins 1 and 2 bearing Cl and NO₂ substituents showed the best efficiency while tetraazaporphyrin 5 was found to be an interesting catalyst for terminal alkene epoxidations.

Many reports deal with alkene epoxidations in the presence of reduced forms of oxygen such as H2O2, ROOH, RCO3H, NaOCI and metalloporphyrins as catalysts^{1,2} but none concern with the comparison of the catalytic activities of porphyrin-like compounds, and only few papers compare the properties of tetraazaporphyrins with those of porphyrins and phthalocyanines.³⁻⁵ With this paper we wish to give a first account on the relative reactivities of manganese-complexes of porphyrins (P), phthalocyanines (Pc) and tetraazaporphyrins (aP), in catalytic alkene epoxidations by means of peracetic acid as primary oxidant, under homogeneous conditions.

In the case of Pc and **aP** it was demonstrated $^{4.6}$ that both reactivities and stabilities in oxidative medium are strongly influenced by their structure, namely: i) presence of isoindole rings instead of pyrrole moieties; ii) presence of electron-withdrawing or electron-donating substituents on the outer skeleton of the macrorings; iii) presence of nitrogen atoms bridging the heterocyclic rings on the 5,10,15,20 positions in comparison with tetraarylporphyrins.

For our purpose, we examined the following catalysts: Mn - tetra-(2,6- dichlorophenyl) - porphyrin (1), Mn - tetra-(2,6-dichloro-3-nitrophenyl) - porphyrin (2), Mn - tetraphenylporphyrin (3), Mn - octanitro - phthalocyanine (4) and Mn - tetra(*tert*-butyl) - tetraazaporphyrin (5).



The free base compounds and their Mn^{III} complexes, each featuring CI⁻ as counteranion, were prepared following known methods.⁷⁸ Peracetic acid was prepared by mixing acetic anhydride and 30%-H2O2 (3:1 v/v) at 25° C, then leaving the mixture for 7-10 days at room temperature. This peracetic acid solution does not contain free hydrogen peroxide, which can alter the catalytic activity of the Mn-complexes due to the occurrence of undesired radical processes; ⁹ furthermore, it was demonstrated that more than 10% excess of H2O2 results in a fast decomposition of both peracetic acid and H2O2 with O2 evolution. Indeed, the catalase activity of the above mentioned Mn-complexes occurs unless the amount of H2O2 is negligible.

It is known that, in the presence of Mn-porphyrins, the heterolysis of *meta*-chloroperbenzoic acid at low temperature gives the high-valent Mn^{IV}-oxo species, which can be isolated and then reacted with alkenes to produce epoxides.¹⁰ Nevertheless, only magnesium monoperoxyphthalate¹¹ and potassium peroxymonosulphate ¹² have been employed for preparative purposes in metallo-porphyrin promoted oxidations, while as far as we know peracetic acid has never been used.

In this preliminary investigation on the reactivity of catalysts 1-5 we have chosen simple reaction conditions in order to easily extend our investigation to kinetic studies (Scheme 1). Thus the reactions were carried out at 20° C in CH₃CN (homogeneous solution) in the presence of a molar excess (1.1 / 1) with respect to the substrate) of 1.3 - 1.7 M peracetic acid solution; the *non catalysed reactions are negligible*, while in the presence of 1-5 reactions occur with a high rate , i. e. for a 1.8×10^{-5} M initial concentration of 1 the full conversion of *cis* - stilbene (6,6 x 10^{-2} M) is achieved in about one hour. It is interesting to point out that the catalytic activity occurs in the absence of axial ligand and/or other co-catalysts generally used with different oxygen donors.^{2,13}



Cis -stilbene was considered as model substrate because its oxidation products are a probe of some mechanistic aspects of the epoxidation.¹⁴ Indeed, a lot of reports can be found in the literature dealing with the mechanisms of metallo-porphyrin promoted epoxidations and several intermediates have been suggested; in the case of Mn^{III} -porphyrins, two species with different oxidising properties have been envisaged, namely a $Mn^{IV}=O$ cation-radical and a $Mn^{V}=O$ oxo-species; their formation depends on several factors, such as solvent polarity and peculiarity of axial ligands, besides the nature of the oxygen donors.^{10,15} The debate can be simply summarized as the occurrence of two main pathways: i) concerted insertion of the oxygen from the high-valent Mn-oxo species into the alkene, which is highly stereoselective; ii) formation of a radical intermediate which gives a mixture of products depending on the life-time of the radical itself.^{10,16} In the particular case of *cis* -stilbene, the exclusive formation of the *cis* - epoxide indicates a concerted mechanism, while the presence of the thermodynamically favoured *trans* - epoxide can be related to the presence of radical intermediates.

In the acetonitrile/peracetic acid mixture, all the catalysts tested gave the *cis* -epoxide as the unique product (NMR and GC data) and their efficiency can be easily extrapolated from the maximum turnover numbers (TN_{max}) reported in Table 1; these data are obtained by using *cis* -stilbene / catalyst ratios in the

range 4,000 - 370,000, the Mn-complex concentrations varying from 1.77×10^{-5} to 1.77×10^{-7} M.

The comparison of the turnover numbers allows to envisage some structural features that dramatically influence the activity of porphinoid catalysts. The highest efficiency is observed with the nitro -substituted porphyrin 2 which is about three times more reactive than 1 and 30 - 70 times more efficient with respect to catalysts 3 - 5.

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 Cata	lysts	Turnovers (TN _{max})	[Catalysts] ₀	Alkene/Cat.	
Р	(1)	55,000	1.77 x 10 ⁻⁷	370,000	
P	(2)	134,000	1.77×10^{-7}	370,000	
P	(3)	1,980	1.77 x 10 ^{.5}	3,700	
Pc	(4)	2,860	1.77 x 10 ^{.5}	3,700	
aP	(5)	3,870	3.00 x 10 ⁻⁶	22,000	

Table 1 - Maximum Turnover Numbers (TN_{max}) in Catalytic cis-Stilbene Epoxidation.^a

a) Reaction conditions as reported in the text; $[cis-stilbene]_0 = 6.6 \times 10^2 M$

Among these last, it is quite surprising to find an higher efficiency for the Mn - tetra (*tert*-butyl) - tetraazaporphyrin (5) with respect to the phthalocyanine 4; indeed 4 bears 8 nitro - groups on its outer rings that, as in the case of porphyrins, should favour the catalytic efficiency, while 5 features slightly electron - donating *tert* - butyl groups. The obvious conclusion is that the presence of benzene rings fused on the pyrrole units produces an undesired effect on catalyst stabilities. Furthermore, 5 is better than the Mn - tetraphenylporphyrin (3), thus indicating that the non pyrrole nitrogen atoms exert a stabilizing effect higher than that produced by *meso* - phenyl rings without electron-withdrawing substituents.

The most demanding steric requirements of catalysts 1, 2 and, partially, 3, with respect to 4 and 5, do not influence their activity in the epoxidation of *cis*-stilbene, but it was found that only flat catalysts like 4, can oxidise *trans*-stilbene too, with the formation of *trans*-stilbene epoxide as single product, although in a lower extent in comparison with the *cis*-isomer (up to 1,400 turnovers). The unreactivity of metalloporphyrins when *trans*-alkenes are used as substrates is well known and is imputed to the interference of one substituent of the alkene with the porphyrin plane. ¹⁷ On this subject it is interesting to note that in the epoxidation of commercial cyclooctene, which is a mixture of about 95 / 5 : *cis* / *trans* isomers, the latter is oxidised only when the very reactive *cis*-alkene is consumed; moreover, when *trans*-stilbene is the substrate in Mn-tetraarylporphyrin catalysed reactions, an unsoluble polymeric material is obtained as major product, the epoxide being less than 10% of the amount of the initial product.

The use of low reacting alkenes is another way to investigate the reactivities of Mn-complexes of macrocycles and the potentialities of the peracetic acid / acetonitrile system. Therefore 1-dodecene was chosen as second model substrate, as we have already done for the epoxidations carried out in the presence of NaOCl or $30\% - H_2O_2$.¹⁸ As it was found with these oxygen donors, the reactivity of 1, 4 and 5, promoted by the peracid solution, also greatly decreased in the case of the terminal alkene and the TN_{max} does not reach 2,000 cycles (Table 2).

Despite this lower TN_{max} a few conclusions can be drawn: i) the electron-withdrawing groups substituted porphyrin 1 is still the best catalyst, but the reactivity differences compared with those of 4 and 5 are not so high as it is in the case of *cis* - stilbene; ii) the decrease of TN_{max} with respect to those found in *cis* -stilbene epoxidations is particularly striking for Mn-complex 1 (30 times lower), while \$ shows only a halved catalytic activity. In particular, the catalytic efficiency of 5 is absolutely comparable with that of 1, TN_{max} being 1.400 and 1.660, respectively. This can be considered as an indication that Mn-tetraazaporphyrins featuring electron-withdrawing substituents on their skeleton might be even better catalysts for terminal alkene epoxidations.

Catalysts		Turnovers (TN _{max})	[Catalysts] ₀	Alkene/Cat.
Р	(1)	1,660	8.3 x 10 ⁶	3,000
Pc	(4)	130	5.6×10^{-5}	450
aP	(5)	1,400	3.0 x 10 ⁻⁶	8,003

Table 2 - Maximum Turnover Numbers (TN_{max}) in Catalytic 1-Dodecene Epoxidation.^a

a) Reaction conditions as reported in the text; $[1-dodecene]_0 = 2.5 \times 10^{-2} M.$

In any case, the turnover values obtained with the peracetic acid system are by far the highest ever obtained in metalloporphine catalysed epoxidations of 1-alkenes; this result, together with the simple reaction conditions and the easy accessibility of the oxidant, make the method here described particularly attractive for preparative purposes.

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