

Transition-Metal Phthalocyanins as Catalysts for Alkene Epoxidation

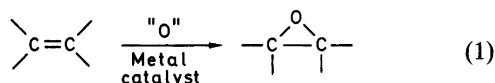
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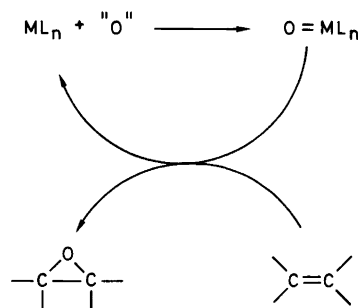
The epoxidation of alkenes catalyzed by transition-metal phthalocyanins has been studied. All the transition-metal [metal = Mn(II), Fe(II), Fe(III), Co(II), Ni(II)] phthalocyanins studied have catalytic properties: the manganese and iron phthalocyanins are most effective when iodosylbenzene is the oxygen donor, whereas cobalt and nickel phthalocyanins are best under phase-transfer catalysis conditions with sodium hypochlorite as the oxygen donor. The epoxidation of *cis*-alkenes leads to a mixture of *cis*- and *trans*-epoxides; the presence of 2,6-di-*tert*-butyl-*p*-cresol in the iron(II) phthalocyanin-catalysed reaction leads to a highly stereospecific epoxidation of *cis*-alkenes. The results are discussed in relation to other transition-metal-catalyzed epoxidations.

The transition-metal-catalyzed epoxidation of alkenes [eqn. (1)] is a field which has undergone extensive development during the last decade.¹



The epoxides formed by this reaction can be converted into a variety of products. Many transition-metal systems have the ability to catalyze the epoxidation reaction and all transition metals starting with group IV (Ti, Zr, Hf) and ending with group I (Cu, Ag, Au) have shown catalytic properties.^{1b} The active catalysts are transition-metal ions, transition-metal oxo and peroxy/peroxide complexes, organotransition-metal complexes, transition-metal clusters and transition-metal surfaces.^{1b}

A variety of oxygen donors have been used for these transition-metal-catalyzed epoxidations, e.g. molecular oxygen, alkyl- and hydro-peroxides, iodosylbenzene, sodium hypochlorite, hydrogen persulfate and oxaziridines.^{1b} The active catalyst operating in these epoxidation reactions varies with the transition metal; at the beginning of the transition-metal series it is a mono- or bi-dentate coordinated metal peroxide or a metal peroxy complex, and from the middle to the end of the transition-metal series it is usually an oxo-metal complex which performs the epoxidation.^{1b} When an oxo-transition-metal complex is involved in the epoxidation, the catalytic properties of the transition metal are due to the fact that it can undergo an oxygen rebound reaction in which the transition metal serves as a relay for the oxygen-atom transfer from the terminal oxidant to the alkene via a reactive oxo-transition-metal intermediate (Scheme 1).

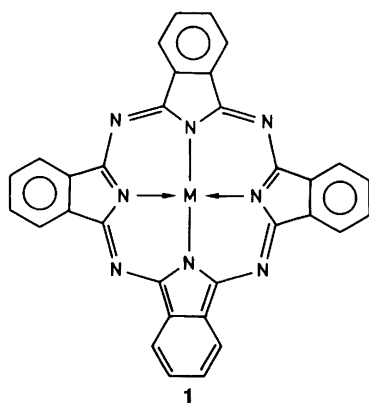


Scheme 1.

The transition-metal porphyrins are a class of complex which has been extensively studied as oxidation catalysts because of their relation to cytochrome P-450 mono-oxygenase.² The catalytic properties have been investigated mainly for manganese and iron porphyrins and the reactive intermediates are suggested to be an oxo-manganese and an oxo-iron porphyrin, respectively.² The transition-metal phthalocyanins (MPcs), **1**, are a class of complexes which has been very intensively studied within many areas in chemistry.³

MPcs have a structure very similar to the transition-metal porphyrins, but MPcs have not been studied to the same extent as catalysts in oxidation reactions and, according to our knowledge, only few examples of MPcs as catalysts for alkene epoxidation have been published.^{3,4,†} There are several reasons why we have chosen to study epoxidation of alkenes catalyzed by MPcs. (i) A general study of the

† Ref. 4 describes the use of MoO₂Pc as a catalyst for the epoxidation of cyclohexene using Bu'OOH as the oxygen donor. This system is different from that described in this paper [see Ref. 1(b)].



catalytic properties of MPcs has not been carried out. (ii) The transition-metal ion in MPcs can be relatively easily exchanged or oxidized which makes it possible to investigate the influence of different transition metals and oxidation states on the catalytic properties (e.g. on epoxide yields and stereoselectivity). In this study the following MPcs have been investigated as epoxidation catalysts: Mn(II)Pc, Fe(III)Pc, Fe(II)Pc, Co(II)Pc and Ni(II)Pc.

Results

The catalytic epoxidation of styrene using the different MPcs and iodosylbenzene or sodium hypochlorite as the oxygen donor has been studied. The ratio between catalyst, styrene and oxygen donor is 1:50:100, and the results are given in Table 1.

It appears from Table 1 that Fe(II)Pc is the best catalyst for the oxidation of styrene to styrene oxide when iodosylbenzene is used as the terminal oxidant; Mn(II)Pc has similar properties, whereas Co(II)Pc and Ni(II)Pc are relatively poor catalysts under the conditions studied. Increasing the concentration of Ni(II)Pc by a factor of ten does not affect the yield of styrene oxide. By-products in the form of benzaldehyde and phenylacetaldehyde are, in some cases, formed in small amounts. Kinetic studies show that Fe(II)Pc is the most effective catalyst. Changing the oxygen donor to sodium hypochlorite under phase-transfer conditions (PTC) with tetrabutylammonium bromide (TBABr) as the phase-transfer reagent in trichloromethane, changes

Table 2. Catalytic oxidation of different alkenes using Fe(II)Pc as the catalyst and iodosylbenzene as the oxygen donor.

Substrate	Epoxide yield/%
α -Methylstyrene	79
α -Phenylstyrene	78
(E)- β -Methylstyrene	63
(Z)- β -Methylstyrene	87
β -Nitrostyrene	<2
(E)-Stilbene	94
(Z)-Stilbene	92
Cyclohexene	67
1-Methylcyclohexene	75
2-Cyclohexenone	<2
Cyclooctene	55
Norbornene	70
1,3-Cyclooctadiene	27 (54 % monoepoxy)
1,5-Cyclooctadiene	26 (5 % diepoxy)
1-Hexene	10
1-Octene	10

the catalytic properties of the MPcs. Under these conditions Co(II)Pc and Ni(II)Pc are the best catalysts, while Mn(II)Pc, Fe(III)Pc and Fe(II)Pc are less effective. Both Co(II)Pc and Ni(II)Pc give a relatively large amount of benzaldehyde. We have compared the catalytic properties of both chloro[5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrinato]-iron(III) and -manganese(III), [Fe(tpp)Cl] and Mn(tpp)Cl] with the MPcs. Under similar experimental conditions as those used in Table 1, the catalytic epoxidation with Mn(tpp)Cl as the catalyst gives 70 % styrene oxide and 5 % phenylacetaldehyde, and with Fe(tpp)Cl as the catalyst 22 % styrene oxide is obtained with iodosylbenzene as the oxygen donor. In terms of the yield of styrene oxide, Mn(tpp)Cl is a slightly better catalyst than Mn(II)Pc, whereas both Fe(III)Pc and Fe(II)Pc are better than Fe(tpp)Cl. Use of *tert*-butyl hydroperoxide as the oxygen donor gives rise to a variety of products and styrene oxide is formed only in small amounts.

With iodosylbenzene as the oxygen donor Fe(II)Pc is the best catalyst; we thus tested Fe(II)Pc as an epoxidation catalyst for a variety of different alkenes under similar conditions. The results, given in Table 2, show that reasonable yields of the corresponding epoxides are obtained.

Table 1. Catalytic oxidation of styrene using different MPcs and different oxygen donors.

Catalyst	Yield/% (PhIO reaction)			Yield/% (NaOCl reaction)		
		PhCHO	PhCH ₂ CHO		PhCHO	PhCH ₂ CHO
Mn(II)Pc	55	8	6	14	3	—
Fe(III)Pc	34	4	—	6	3	—
Fe(II)Pc	59	6	5	17	6	—
Co(II)Pc	7	—	—	58	11	—
Ni(II)Pc	<2	<2	—	33	10	—
10×Ni(II)Pc	<2	2	—			

When electron-withdrawing groups are attached to the double bond (e.g. 2-cyclohexenone) low yields of the corresponding epoxides are obtained; these results might indicate that the oxygen which is transferred to the double bond is of electrophilic character. The reaction is non-stereospecific as epoxidation of *cis*-alkenes gives a mixture of both the corresponding *cis*- and *trans*-epoxides. The *cis/trans* ratio is dependent on the transition metal present in MPcs and the oxygen donor used.

Table 3 gives the results obtained for the epoxidation of (*Z*)- β -methylstyrene and (*Z*)-stilbene using the different MPcs and iodosylbenzene or sodium hypochlorite as the oxygen donor. The trends observed for epoxidation of styrene with iodosylbenzene and sodium hypochlorite with the different MPcs as catalysts are also found for epoxidation of (*Z*)- β -methylstyrene and (*Z*)-stilbene. Using iodosylbenzene as the oxygen donor affords a higher *cis/trans* ratio compared with sodium hypochlorite. The highest *cis/trans* ratio is obtained with Fe(II)Pc as catalyst with both iodosylbenzene and sodium hypochlorite as oxygen donors. The presence of donor ligands, such as pyridine or *N*-methylimidazole does not increase the yields of epoxide. Addition of 10 equivalents of these nitrogen bases relative to the catalyst leads to a decrease in the yield of epoxides, the most drastic decrease being found for Fe(II)Pc where the addition of *N*-methylimidazole leads to only 16% styrene oxide compared with 59% in its absence. The addition of further amounts of nitrogen bases leads to a further decrease in the yield of epoxide. The stereospecificity of the catalytic epoxidation reaction is dependent on the presence of nitrogen bases as both (*Z*)- β -methylstyrene and (*Z*)-

stilbene give lower *cis/trans* epoxide ratios in the presence of *N*-methylimidazole or pyridine than in the absence of these donor ligands.

We have found that the presence of 2,6-di-*tert*-butyl-*p*-cresol, **2**, has a significant effect on the yield and the stereospecificity of the oxygen transfer especially when Fe(II)Pc is used as the catalyst and iodosylbenzene as the oxygen donor. The presence of **2** during the reaction leads to an almost stereospecific epoxidation when (*Z*)-stilbene is epoxidized (*trans*-stilbene oxide is produced in less than 2% yield) compared with a *cis/trans* ratio of 7.6 when the reaction is carried out in the absence of **2**. Compound **2** also has an effect on the stereospecificity when Mn(II)Pc and Fe(III)Pc are used as catalysts and iodosylbenzene as the oxygen donor, but the effect is not so pronounced compared with Fe(II)Pc as catalyst. In all of these cases an increased yield of epoxide is found.

The catalytic epoxidation of e.g. styrene by different MPcs with sodium hypochlorite as the oxygen donor under PTC is dependent on the phase-transfer catalyst used. Other tetraalkylammonium bromides when used as phase-transfer catalysts give results similar to TBABr, whereas the yield of epoxide is reduced when mixed alkyl-benzyl ammonium salts are employed. It is also found that for the epoxidation of alkenes under PTC conditions, the addition of nitrogen-donor ligands causes no change in the *cis/trans* ratio, but leads to a decrease in the yield of the epoxide.

The yield of the epoxide is strongly dependent on the solvent. Epoxidation of styrene with Fe(II)Pc as the catalyst and iodosylbenzene as the oxygen donor, after 2 h, gave less than 2% yield of styrene oxide in solvents such as

Table 3. Yields/% of the products from the catalytic oxidation of (*Z*)- β -methylstyrene and (*Z*)-stilbene using different MPcs and iodosylbenzene or sodium hypochlorite as oxygen donors.

	<i>(Z)</i> - β -methylstyrene			
	Iodosylbenzene		Sodium hypochlorite	
	Epoxide/%	<i>cis/trans</i> ratio	Epoxide/%	<i>cis/trans</i> ratio
Mn(II)Pc	40	2.1	12	1.0
Fe(III)Pc	40	4.0	8	0.77
Fe(II)Pc	87	8.7	18	1.2
Co(II)Pc	13	0.2	30	0.15
Ni(II)Pc	4	—	26	0.18
	<i>(Z)</i> -stilbene			
	Iodosylbenzene		Sodium hypochlorite	
	Epoxide/%	<i>cis/trans</i> ratio	Epoxide/%	<i>cis/trans</i> ratio
Mn(II)Pc	50	2.3	24	1.4
Fe(III)Pc	70	7.8	20	1.5
Fe(II)Pc	86	7.6	40	3.0
Co(II)c	17	0.2	88	0.14
Ni(II)Pc	<2	—	52	0.17

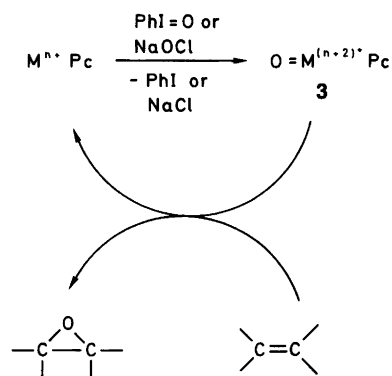
carbon disulfide, hexane, dimethyl formamide, diethyl ether, 10–15 % in methanol or ethanol, and 35–59 % in benzene, dichloromethane or trichloromethane.

Discussion

The ability of MPcs to act as catalysts for alkene epoxidation depends on the transition metal present in the MPcs and the oxygen donor used. When iodosylbenzene is the oxygen donor, Fe(II)Pc is the best catalyst and the yield of epoxide can be improved by increasing the amount of Fe(II)Pc or iodosylbenzene. The catalytic properties of Fe(II)Pc and Fe(III)Pc are different from those found for the iron porphyrins. Fe(tpp)Cl acts as a catalyst for the stereoselective epoxidation of alkenes;^{2,5} (*Z*)-alkenes are epoxidized to the corresponding *cis*-epoxides, whereas the (*E*)-alkenes are inert under the same conditions.⁵ In contrast with Fe(tpp)Cl, Fe(III)Pc and Fe(II)Pc catalyze the epoxidation of both (*Z*)- and (*E*)-alkenes, but the (*Z*)-alkenes give both the corresponding *cis*- and *trans*-epoxides, which might indicate that the electronic properties of the oxo-iron species in the oxo-iron phthalocyanins are different from those in the oxo-iron porphyrins, or that the periphery around the iron atom influences the reaction course. Fe(II)Pc has been found to act as a general catalyst for alkene epoxidation for a series of alkenes and relatively good yields of the corresponding epoxides are obtained, except for alkenes with electron-withdrawing groups (Table 2). The oxidation state in the iron phthalocyanins affects the yield of epoxide: a lower yield is obtained when Fe(III)Pc is used as the catalyst compared with Fe(II)Pc (Tables 1 and 3). On the other hand, the stereospecificity is relatively independent of the oxidation state of iron (Table 3). The catalytic properties of Mn(II)Pc are not as effective as Fe(II)Pc with both iodosylbenzene and sodium hypochlorite as oxygen donors under the conditions studied (Tables 1 and 3). With iodosylbenzene as the oxygen donor both Co(II)Pc and Ni(II)Pc are relatively poor epoxidation catalysts compared with Mn(II)Pc and Fe(II)Pc; the Co(II)Pc-catalyzed epoxidation gives a relatively low yield of epoxide when different alkenes are chosen as substrates. The epoxidation of (*Z*)- β -methylstyrene and (*Z*)-stilbene by the Co(II)Pc/iodosylbenzene system gives essentially the corresponding *trans*-epoxides, which is in contrast with the results obtained with Co(II)-bis-salicylamide as catalyst, where the oxygen transfer from iodosylbenzene to the alkene proceeds with high stereospecificity.^{6a} The Ni(II)Pc is a poorer catalyst than Co(II)Pc, and even a tenfold increase of the catalyst did not increase the yield of epoxide above 2 % (Table 1). Only a few examples have been reported with Ni(II) complexes as a catalyst for alkene epoxidation, e.g. the complexation of Ni(II) to tetraaza macrocycles affords a system which has catalytic properties.⁷ The product pattern for the MPcs changes when sodium hypochlorite is the oxygen donor under PTC. In this case Co(II)Pc is the best catalyst and, according to our knowledge, this is the first time that a Co(II) complex has

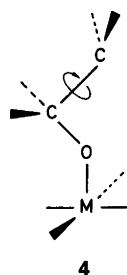
been used as a catalyst for alkene epoxidation with sodium hypochlorite as the oxygen donor (Tables 1 and 3). Ni(II)Pc can also act as a catalyst for alkene epoxidation with sodium hypochlorite under PTC, and both Co(II)Pc and Ni(II)Pc have been found to be better catalysts than Mn(II)Pc, Fe(III)Pc and Fe(II)Pc (Tables 1 and 3). The epoxidation of styrene carried out under these conditions affords a relatively large amount of benzaldehyde as a by-product (Table 1). Both the Co(II)Pc and Ni(II)Pc/sodium hypochlorite systems are able to catalyze the epoxidation of different alkenes, but the reaction is non-stereospecific as mainly the *trans*-epoxides are obtained from epoxidation of (*Z*)-alkenes. The results found for the epoxidation of (*Z*)-alkenes catalyzed by Ni(II)Pc are in good agreement with those recently published in which Ni(II)salen/sodium hypochlorite was used as catalyst/oxygen donor.⁸ Comparing the results obtained for the epoxidation of alkenes catalyzed by MPcs and with iodosylbenzene or sodium hypochlorite as oxygen donors it appears that different results are obtained. Iodosylbenzene as oxygen donor works best for manganese and iron phthalocyanin as catalyst, whereas sodium hypochlorite is best for cobalt phthalocyanin under PTC. The oxygen source (iodosylbenzene or sodium hypochlorite) also influences the stereospecificity of the epoxidation: a lower *cis/trans* epoxide ratio is found when sodium hypochlorite is used compared with iodosylbenzene, with manganese and iron phthalocyanins as catalysts, whereas both Co(II)Pc and Ni(II)Pc give the same *cis/trans* epoxide ratio, independent of the oxygen source.

There is relatively good evidence that the first step in the reaction of oxygen donors, such as iodosylbenzene and sodium hypochlorite, with metal–ligand complexes is the formation of an oxo-metal–ligand complex.* A similar type of reaction is probably also operative with the MPcs (Scheme 2) leading to a two-electron oxidation of the metal, **3**. The species **3** then transfers the oxygen atom to the alkene (Scheme 2). The oxygen-transfer step from **3** to



Scheme 2.

* See Refs. 1 and 2 for a discussion of the formation of oxo-metal–ligand complexes in this type of oxidation reaction.



4

the alkene takes place non-stereospecifically, indicating that, along the reaction path, free rotation around the carbon-carbon bond is possible; a possible structure for the intermediate for the oxygen-transfer step is shown in 4.

The presence of 2 during the Fe(II)Pc-catalyzed reaction affords a virtually stereospecific epoxidation of (*Z*)-stilbene, which might indicate that 2 changes the electronic properties of the oxo-iron(IV) phthalocyanine leading to an intermediate which is able to transfer the oxygen in a stereospecific manner. One could, in this case, envisage a reaction path in which both carbons in the alkene interact with the oxygen in the oxo-iron(IV) phthalocyanine or possibly the involvement of an iron cyclooxethane intermediate.¹⁰

Experimental

¹H and ¹³C NMR spectra were recorded on a Varian Gemini 200 Spectrometer. SiMe₄ was used as an internal standard. Mass spectra were recorded on a Micro-Mass 7070F or Trio-2 spectrometer (GC/MS) operating at 70 eV using a direct inlet. GLC was recorded on an HP5890; column: OV-1.

Materials. Fe(II)Pc, Co(II)Pc and Ni(II)Pc are commercially available. Mn(II)Pc and Fe(III)Pc were synthesised according to the literature.⁹

General procedure for the epoxidation of alkenes. The alkene (1.5 mmol) and 3.0 × 10⁻² mmol of the MPc were dissolved in 10 ml CHCl₃. 3.0 mmol of iodosylbenzene were then added and the reaction mixture was stirred for 24 h. In some instances, 2,6-di-*tert*-butyl-*p*-cresol, pyridine or *N*-methylimidazole were added to the reaction mixture.

After the reaction mixture had been filtered through

Celite to remove the excess of iodosylbenzene, it was analyzed by ¹H and ¹³C NMR spectroscopy or GC-MS. The ¹H and ¹³C NMR data of the epoxides are available from the literature.¹¹

Oxidation of alkenes by MPc and sodium hypochlorite under phase-transfer conditions. The alkene (1.5 mmol), 0.15 mmol of the phase-transfer catalyst and 3 × 10⁻⁵ mol of the MPc were dissolved in 10 ml CHCl₃. In some instances, pyridine or 2,6-di-*tert*-butyl-*p*-cresol were then added. The resulting solution was mixed with 5 ml of 2 M aqueous sodium hypochlorite and stirred for 24 h. The CHCl₃ phase was then removed and extracted several times with water. After the organic phase had been dried with Na₂SO₄ the reaction mixture was analyzed as above.

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