

Comparative ^1H NMR and UV-Visible Studies of Polyene Polymer Epoxidations Catalyzed by Iron(III), Manganese(III) and Chromium(III) Porphyrins[†]

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ABSTRACT: The catalytic epoxidation of *cis*-polybutadiene was studied in two-phase systems, $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ and $\text{PhIO}(\text{solid})/\text{CH}_2\text{Cl}_2$, using chlorochromium(III), chloromanganese(III) and chloroiron(III) tetraphenylporphyrin complexes as catalysts. Comparison of the catalytic activity of these three catalysts showed that the manganese porphyrin is the most suitable catalyst for this reaction. The results are based on reaction product ratios as determined by ^1H NMR. UV-Visible spectroscopy allowed monitoring of the metalloporphyrin evolution during the catalytic reaction. © 1998 John Wiley & Sons, Ltd.

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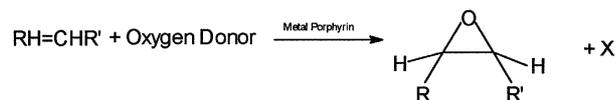
KEYWORDS: chlorochromium(III)tetraphenylporphyrins; manganese(III)tetraphenylporphyrins; iron(III)tetraphenylporphyrins; catalysis; epoxidation; polyene polymers

INTRODUCTION

In the last decades there has been increasing interest in the field of catalytic oxidation of unfunctionalized olefins by metalloporphyrins [1]. This is due to attempts to mimic enzymes (such as cytochrome P-450 [2]), able to perform intrinsically difficult oxidations at ambient temperature, by using simple synthetic models to produce valuable chemicals.

The epoxidation of alkenes is an important industrial process. Recent developments of metal-catalyzed epoxidations has encouraged further attempts to develop more selective and commercially significant epoxidation reactions [3]. Among the transition metal oxygen-transfer catalysts, metalloporphyrins present attractive advantages [1, 4–9].

They provide a robust four-coordinate ligand which can resist destruction and has potential chemo-, regio- and stereoselectivity properties. It is, therefore, of great interest to study the mechanism by which metalloporphyrins transfer an oxygen atom to alkenes (Scheme 1).



Scheme 1. Oxygen transfer processes.

Herein, we present the oxygenation of *cis*-polybutadiene by using metalloporphyrins as catalysts. We also present a comparison study and the suitability of three catalysts with different metal ions in association with two different oxygen donors, iodosylbenzene and sodium hypochlorite, Fig. 1.

Our results provide information which will help design specific synthetic oxidation processes. Comparison of these with the literature data is expected to further delineate the epoxidation mechanism of polyalkenes.

[†]This work is dedicated to the memory of our friend, Dr Michel Mometeau.

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EXPERIMENTAL SECTION

Materials

cis-Polybutadiene (Aldrich lab/chunk, 98% *cis*), benzyldimethyltetradecylammonium chloride dihydrate (Aldrich 99+%), *m*-chloroperbenzoic acid (*m*-CPBA) (Fluka assay ~ 55%), pyridine (99+%) and iodobenzene diacetate (98% Aldrich) were used as received. Methylene chloride (Riedel de Haën, pro analysi) was distilled over CaH₂ under argon or nitrogen. Sodium hypochlorite was obtained from Riedel de Haën, c. 12–13% Cl active, and titrated by the iodometric method. Iodosylbenzene was prepared according to a literature method [10] by hydrolysis of iodobenzene diacetate with NaOH.

Porphyrins

Chromium(III) *meso*-tetraphenyl porphyrin chloride [11a] manganese(III) *meso*-tetraphenyl porphyrin chloride [11b] and iron(III) *meso*-tetraphenyl porphyrin chloride [11c] were prepared as described in the literature.

Instruments

¹H NMR spectra were measured in CDCl₃ solutions on a Bruker FT-250 apparatus with chemical shifts reported in ppm relative to tetramethylsilane (TMS) or the central chloroform peak fixed at 7.26 ppm. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer or a 'home made' Oriol diode-array visible spectrophotometer (sample concentration 7.7 × 10⁻³ mmol l⁻¹).

Epoxidation Procedures

All the reactions were carried out at room temperature in the air, inside a 50 ml round bottle equipped with a stirring bar (note: it is well established that oxygen from the air is not involved in the above reaction process).

Epoxidation with Iodosylbenzene. *cis*-Polybutadiene (50 mg (0.926 mmol)) was dissolved in 10 ml of methylene chloride. Then, 0.023 mmol of the metalloporphyrin M^{III}(TPP)Cl (where M = Cr, Mn and Fe) was added to the solution. Finally, 0.6 g (2.85 mmol) of iodosylbenzene was introduced and the reaction mixture was stirred for 24 h. Stirring was stopped, prior to each aliquot (0.3 ml) withdrawal from the reaction mixture. The solvent was removed, the residue was dissolved in CDCl₃ (0.4 ml) and its ¹H NMR spectrum was recorded. The above described procedure was used to check the conversion of *cis*-polybutadiene to the oxygenated products.

Epoxidation with Sodium Hypochlorite. *cis*-Polybutadiene (50 mg (0.926 mmol)) was dissolved in 10 ml of methylene chloride. To the solution of metalloporphyrin (0.023 mmol), benzyldimethyltetradecylammonium chloride (20 mg, 0.049 mmol) was added. Then, 20 ml of sodium hypochlorite was introduced to the reaction mixture. After 24 h the two layers were separated, an aliquot (0.3 ml) was taken from the reaction mixture and was dried with anhydrous magnesium sulfate. Finally, the solvent was removed and from the residue the ¹H NMR spectrum was obtained in CDCl₃.

Table 1. Catalytic conversion of *cis*-polybutadiene to the corresponding polyepoxide by three catalysts and iodosylbenzene (reaction time: 24 h)

Catalyst/ polymer (%)	Pyridine/ catalyst	Cr ^{III} (TPP)Cl			Mn ^{III} (TPP)Cl			Fe ^{III} (TPP)Cl		
		Yield	<i>cis</i> -	<i>trans</i> -	Yield	<i>cis</i> -	<i>trans</i> -	Yield	<i>cis</i> -	<i>trans</i> -
1.5	–	21.9	2.6	19.3	73.8	40.5	33.3	33.6	11.5	22.1
1.5	10/1	22.7	2.1	20.6	82.9	53.7	29.2	34.7	14.3	20.4
2.5	–	27.8	4.8	23.0	86.3	59.7	26.6	40.0	14.0	26.0
2.5	10/1	39.7	7.0	32.7	92.2	68.1	24.1	41.7	17.1	24.6
2.5	15/1	48.4	8.0	40.7	100.0	72.1	27.9	47.4	21.8	25.6

Table 2. Catalytic conversion of *cis*-polybutadiene with Mn^{III}(TPP)Cl as the catalyst and sodium hypochlorite (reaction time: 24 hrs)

Catalyst/ polymer (%)	Pyridine/ catalyst	Conversion (%)	Total epoxide yield (%)	<i>cis</i> -Epoxide (%)	<i>trans</i> -Epoxide (%)
1.5	–	67.9	35.5	28.3	7.2
1.5	10/1	70.0	40.5	36.0	4.5
2.5	–	84.3	60.5	57.6	2.9
2.5	10/1	89.0	64.6	61.0	3.6
2.5	15/1	93.0	68.3	65.9	2.4

UV-Visible Procedure or Time-resolved Experiments

The same experiments were repeated on a microscale, under exactly the same conditions as described above, at room temperature inside a UV-vis cell. In a typical experiment after dissolution of the *cis*-polybutadiene, the catalyst was added to the solution. Finally the oxygen donor was introduced to the above solution and immediately a series of 20–25 spectra were recorded.

RESULTS AND DISCUSSION

The two spectroscopic methods described below exhibit very interesting features in terms of the information they provide on the epoxidation process of the *cis*-polybutadiene: by ¹H NMR, one is in a position to carry out controls on the substrate in the presence of the catalyst without any perturbation; by UV-vis, one can check any changes in the catalyst in addition to any species generated (again in the presence of the substrate).

¹H NMR Analysis

First of all, the reaction of *cis*-polybutadiene with *m*-CPBA, which itself is an epoxidizing agent, was carried out in order to identify the peaks of the polyepoxide formed [12]. It is well known that the epoxidation of olefins by this agent is stereospecific (*cis*-olefins give only *cis*-epoxides). On this basis, we have in our hands a process for determining the ratio of *cis*-/*trans*-epoxides, as mentioned below. Blank experiments were carried out without the catalyst for both oxygen donors, in order to control the feasibility of the epoxidation reaction by the other chemicals

used in the reaction mixture. All reactions were checked periodically by ¹H NMR spectroscopy. Our investigations have shown that no appreciable epoxidation reaction occurred after 24 h.

The conversion of *cis*-polybutadiene catalyzed by Cr^{III}(TPP)Cl, Mn^{III}(TPP)Cl and Fe^{III}(TPP)Cl in the presence of iodobenzene are reported in Table 1. Table 2 makes the distinction between the conversion of *cis*-polybutadiene to the oxygenated products and the polyepoxide yield (when sodium hypochlorite is used as oxygen donor), only in the case of Mn^{III}(TPP)Cl (as there is no epoxidation reaction with the other two catalysts). The main difference between these two oxygen donors was observed in the reaction products: with iodobenzene only epoxides (*cis*- and *trans*-) formed, while with sodium hypochlorite, in addition to the epoxides, a few other

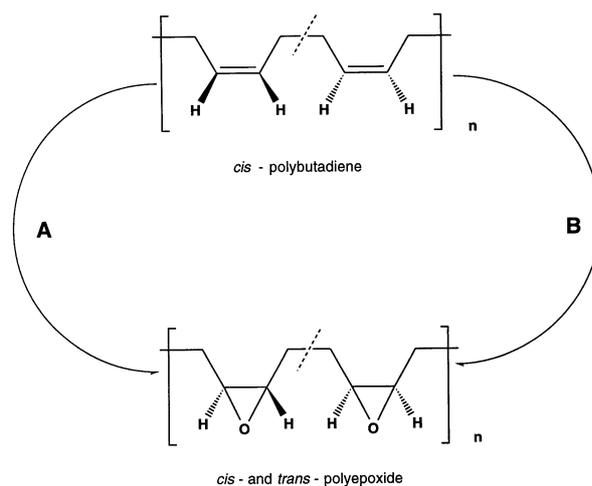


Fig. 1. Epoxidation reaction of *cis*-polybutadiene with (A) PhIO and (B) NaOCl (catalyst is Mn^{III}(TPP)Cl in CH₂Cl₂ with or without pyridine for both cases).

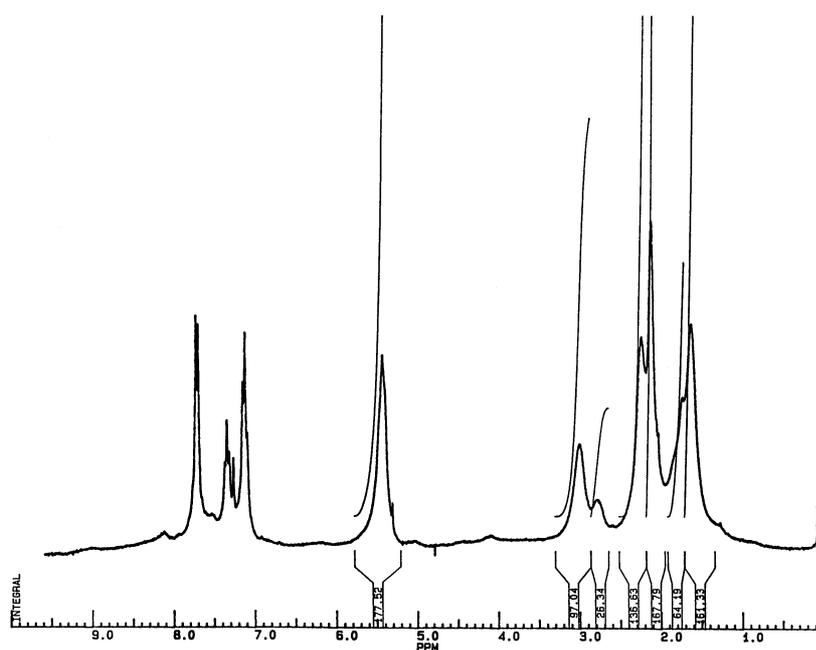


Fig. 2. ^1H NMR spectrum of *cis*-polybutadiene with PhIO as the oxygen donor before 24 h, where the *cis*- and *trans*- forms are present together with the starting material.

products formed as discussed below on the basis of our NMR experiments. As shown in Tables 1 and 2, $\text{Mn}^{\text{III}}(\text{TPP})\text{Cl}$ acts as a very good catalyst with both oxygen donors [13].

When PhIO was used as the oxygen donor, the polyepoxide was the only product detected by ^1H NMR

analysis. The conversion of *cis*-polybutadiene to the corresponding polyepoxide was estimated by integration of the vinylic protons of the polymer, which are assigned to 5.3 ppm, and the $-\text{CH}-$ protons of the epoxide, which were assigned to 3 and 2.8 ppm for the *cis*- and the *trans*-epoxide, respectively (Fig. 2).

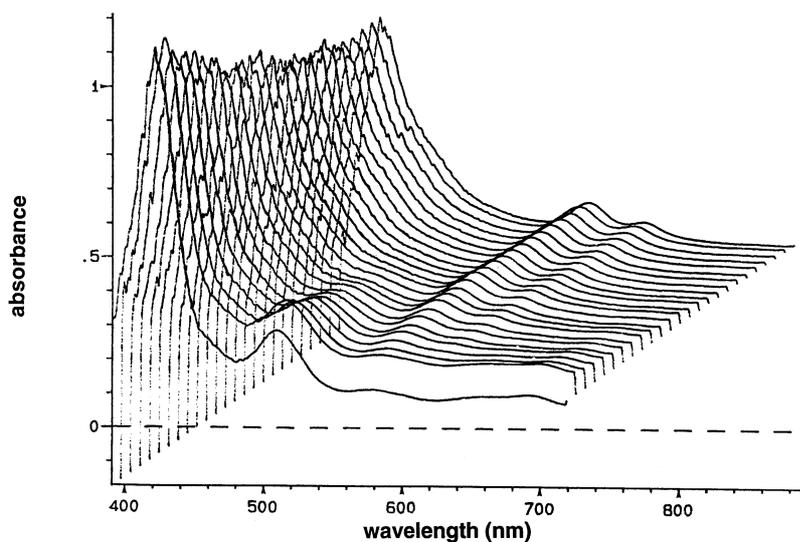


Fig. 3. Time-resolved spectra of the $\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}$ epoxidation reaction by NaOCl ; interval time: 60 s.

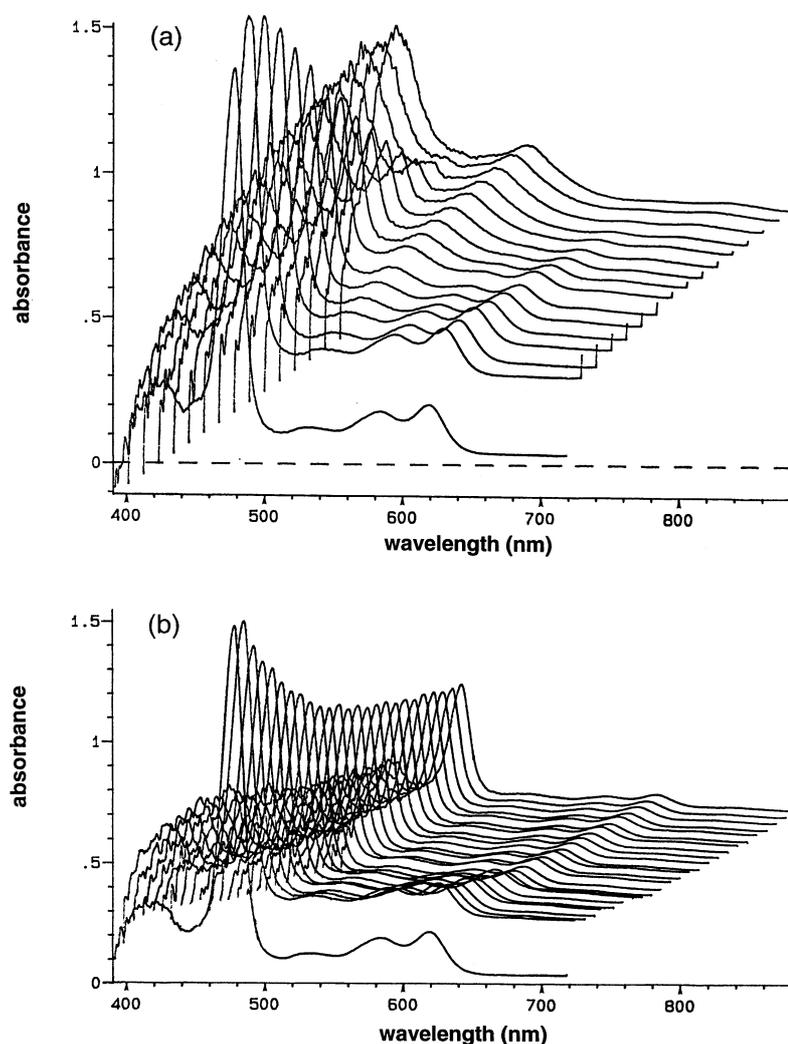


Fig. 4. Time-resolved spectra of the $\text{Mn}^{\text{III}}(\text{TPP})\text{Cl}$ epoxidation reaction by (a) PhIO; interval time: 5 s, and (b) NaOCl; interval time: 60 s.

For $\text{Mn}^{\text{III}}(\text{TPP})\text{Cl}$, the *cis*-epoxide was the major product (see Table 1). The ratio of *cis*-/*trans*- increased by increasing the ratio of catalyst/polymer and/or pyridine/catalyst (from *cis*-/*trans*- 1.2/1 for catalyst/polymer 1.5% without pyridine to 2.6/1 for catalyst/polymer 2.5% and pyridine/catalyst 15/1). It should be noted here that the addition of more than 15 equivalents of pyridine, with respect to the catalyst, results in a lower conversion of *cis*-polybutadiene. This is probably due to the fact that the major species in solution at these conditions is the bis-pyridine adduct $[\text{M}^{\text{III}}(\text{TPP})(\text{pyridine})_2]$. Hence, no axial position is available for the activation of the oxygen atom donor, and consequently the catalyst becomes inactive. The same production of *cis*- and *trans*-epoxides

has also been observed for Cr(III) and Fe(III) catalysts with the only exception being in these cases that the conversion to polyepoxides is poor (Table 1).

When NaOCl is used as the oxygen donor, the ratio of *cis*-/*trans*- epoxide was much greater than the corresponding ratio in the case of PhIO (from 3.9/1 for catalyst/polymer 1.5% to 27.5/1 for catalyst/polymer 2.5% and pyridine/catalyst 15/1) with $\text{Mn}^{\text{III}}(\text{TPP})\text{Cl}$. Moreover, in addition to the above peaks which correspond to the polyepoxide, two more peaks were observed at 3.1 ppm and 3.3 ppm. These two peaks disappeared on addition of D_2O . This is a strong indication that these peaks correspond to labile protons present on the products formed. A reasonable explanation for the aforementioned could be provided

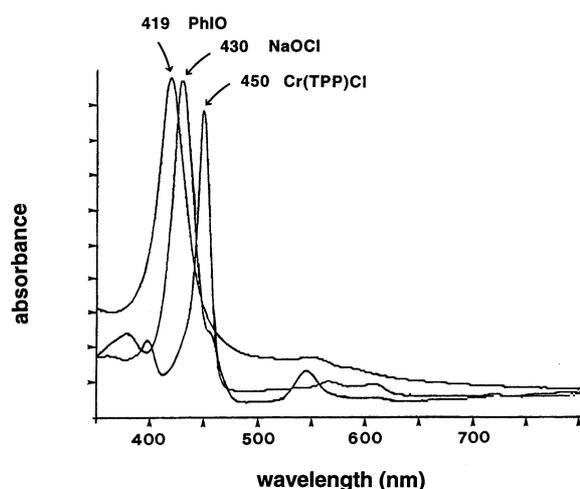


Fig. 5. UV-vis spectra of $\text{Cr}^{\text{III}}(\text{TPP})\text{Cl}$ and the epoxidation reaction with (a) PhIO and (b) NaOCl.

if we consider that a basic hydrolysis of the oxirane ring formed occurs since the reaction is carried out at basic pH (sodium hypochlorite solution). As a result, formation of hydroxy protons could not be excluded.

Chloroiron(III) tetraphenylporphyrin was used as a catalyst of the epoxidation reaction only when PhIO was the oxygen donor. In comparison with the corresponding manganese catalyst (see Table 1), the iron porphyrin is a less efficient catalyst. When NaOCl was used as the oxygen donor there was no epoxidation reaction. Similar results were observed for the other olefin oxygenation reactions, where in the presence of pyridine or imidazole ligands, $\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}$ showed no activity as an epoxidation catalyst with sodium hypochlorites [14a,b]. However, it was found that only the $\text{Fe}(\text{III})$ 'picket fence' porphyrin in the presence of bulky axial ligands [14a] and sterically hindered iron porphyrins [14b] is catalytically active.

Product analysis in the first 24 h showed 33–47% conversion of *cis*-polybutadiene to the corresponding polyepoxide. In contrast to the manganese porphyrin, the *trans*-epoxide is the major product and only when catalyst/polymer 2.5% and pyridine/catalyst 15/1, is the ratio of *cis*-/*trans*- about 1/1.

The same behavior as iron was seen when $\text{Cr}^{\text{III}}(\text{TPP})\text{Cl}$ was used as a catalyst. The *trans*-epoxide is the major product, but the ratio *cis*-/*trans*- is much lower when compared to the iron porphyrin. According to the above observation and the literature data, we deem that this is due to distinctly different mechanisms for $\text{Fe}(\text{III})$ [15a], and $\text{Cr}(\text{III})$ [15b], which take

place, even if the comparison ratios are similar. This is discussed in the next section.

UV-Visible Analysis

$\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}$. Reaction mixtures of both epoxidation processes, A and B, were examined by time-resolved experiments by UV-vis spectroscopy. A dramatic destruction of the catalyst was observed in case A (PhIO as oxygen donor). This is not the case for process B (NaOCl as oxygen donor) where the degradation of the catalyst is very slow. Few differences on the Q bands indicate ligand exchange of the initial form of catalyst by the oxygen donor (Fig. 3).

Formation of *N*-alkylporphyrin is not observed with this spectroscopic method as has been mentioned for the epoxidation of 1,2-substituted olefins [16]. High valent iron-oxo porphyrins are very reactive species and have been observed only at very low temperatures [17].

From these results we can only conclude that the low reactivity of $\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}$ is due to the oxidative degradation of the porphyrin ring. Finally as a prediction, if we desire to perform a better conversion of *cis*-polybutadiene we should use more sterically hindered porphyrin rings of more robust catalysts.

$\text{Mn}^{\text{III}}(\text{TPP})\text{Cl}$. For both oxygen donors the UV-vis time-resolved spectra for the transformation of *cis*-polybutadiene were studied. (Fig. 4). When PhIO was used as the oxygen donor we observed a change in the catalyst to the Mn-oxo species, with characteristic peaks at 430 nm (Soret band) and a broad band at 526 nm. The latter band is characteristic of monomer Mn(IV) porphyrins [18]. In the case where NaOCl was used as oxygen donor, this transformation was much more slower (time intervals were 5 and 60 s with PhIO and NaOCl, respectively). Taking into account the fact that well-defined but different Mn(IV) and Mn(V)-oxo porphyrins [18, 19] possess a Soret band in the same region (425 ± 5 nm) it is difficult to reach conclusions about the oxidation state of manganese. It is well known that Mn(V)-oxo porphyrin is unstable [19] and has not been isolated at ambient temperature. Mn(IV)-oxo porphyrin is relative stable as compared to Mn(V) and many Mn(IV)-oxo porphyrins have been isolated and characterized [18]. According to the above-mentioned results, we can presume that in our experiments we observe Mn(IV) rather than Mn(V) species, as we run these experiments at room temperature.

Recently it has been shown that the *trans*-epoxide resulting from a radical type oxidation probably arises from contamination of the manganese(V)-oxo porphyrin by Mn(IV)-oxo porphyrin [19a, 20]. The Mn(IV)-oxo porphyrin results from decomposition of Mn(V)-oxo porphyrin and from the reaction of Mn(V)-oxo porphyrin with Mn(III) porphyrin. Both Mn(IV) and Mn(V)-oxo porphyrins are capable of transferring an oxygen atom to alkenes but the alkene epoxidation mechanisms are different.

Cr^{III}(TPP)Cl. With Cr^{III}(TPP)Cl, we are able to confirm, by UV-vis spectroscopy in an unambiguous way, the formation of the Cr(IV)-oxo porphyrin [21] complex (Soret band at 430 nm) when NaOCl (case B, Fig. 1) was used as the oxygen donor (Fig. 5). When PhIO was used as the oxygen donor (case A, Fig. 1) a shift of the Soret band from 450 nm (Cr(III)) to 419 nm was observed which corresponds to Cr(V) [22] (Fig. 5). These results partially confirm the fact that in case A conversion to polyepoxide (formation of Cr(V)-oxo species) occurs which is not the case with process B (formation of Cr(IV)-oxo species).

It is well known that chromium(IV)-oxo complexes are stable molecules. O=Cr(IV) (TPP) has been prepared by the oxidation of Cr(III) derivatives [23] with NaOCl or PhIO [21]. This metal oxo complex is inert toward olefins. However, the product of the one-electron oxidation of O=Cr(IV) (TPP) is reactive towards olefins. The mechanism of oxygen transfer from high valent chromium complexes to olefins has been studied in detail [24]. In our case, with NaOCl, a slow transformation of the catalyst to the Cr(IV)-oxo complex was observed with no active behavior towards the epoxidation of *cis*-polybutadiene. The above observation is in agreement with the reported data in the case of Cr(IV) species.

Finally, with iron and chromium porphyrins we observed complete destruction of the catalyst at the end of the reaction, which was not the case when manganese porphyrin was used as the catalyst.

CONCLUSIONS

From the results presented here, it is obvious that manganese porphyrin is the best catalyst as opposed to the iron or chromium analogs of this porphyrin ligand. So, using one of most common metalloporphyrins and pyridine as the axial ligand we can achieve complete conversion of a polyene polymeric material to the corresponding epoxide.

The difference among these three catalysts is probably due to different mechanisms operating in each case. This, in turn, is due to the nature of the metal ion as well as the stability or instability of the intermediate species involved in the reaction mechanism. From those differences emerges a variable ratio of *cis*- and *trans*-polyepoxides.

The choice of the oxygen donor is a crucial factor in obtaining high conversions of *cis*-polybutadiene in a few hours.

Finally, the influence of other substituted pyridines and third-generation porphyrins is an intriguing puzzle currently under investigation in our laboratory.

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