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# Olefin oxidation with dioxygen catalyzed by porphyrins and phthalocyanines intercalated in α-zirconium phosphate

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**Abstract**

Oxidation of cyclohexene and *cis*-stilbene with dioxygen in presence of metal phthalocyanines or metal tetraphenylporphyrins complexes intercalated in α-zirconium phosphate and isobutyraldehyde were studied. The degradation of free metal complexes in solution in the reaction media was verified. It was observed that the matrix protects the metal complexes from degradation and the activity of the catalytic system is preserved. Oxidation of cyclohexene with intercalated complexes gave epoxide as the predominant product, while allylic oxidation products were obtained in smaller proportion and the product distributions depended on the identity of the individual metal complexes. Since the addition of a free radical inhibitor stops the reaction, a free radical mechanism should be present. Oxidation of *cis*-stilbene with intercalated metal complexes gives different ratios of *cis*- to *trans*-stilbene oxide and of benzaldehyde which depend on the intercalated metal complex, suggesting that in addition to the free radicals there is another active oxidizing agent. 

*Keywords:* Biomimetic catalysis; Dioxygen reductive activation; Phthalocyanines and tetraphenylporphyrins intercalated; α-Zirconium phosphate; Olefin epoxidation

## 1. Introduction

The ability of cytochrome P-450 to activate oxygen has inspired a multitude of studies that involve metalloporphyrins and metallophthalocyanines as potential catalysts for the selective oxidation of alkanes and alkenes [1–3]. The requirement of an electron source to activate dioxygen has prompted Tabushi [4] to design and implement a series of model monooxygenase systems based on metalloporphyrins to induce dioxygen activation in combination with reducing agents such as sodium tetra-boron hydride ($NaBH_4$), colloidal $Pt/H_2$, ascorbates and aldehydes have also been used [5]. Monooxygen transfer reagents, such as iodosylbenzene (PhIO), hydrogen peroxide ($H_2O_2$) and *tert*-butylhydroperoxide (*t*-BuOOH) have been employed [6].

The conversion of hydrocarbons into oxygenated products is a very important process that has recently received much attention, principally using porphyrins and phthalocyanines as catalysts in solution [7,8]. Nevertheless, there are strong indications that phthalocyanines and porphyrins have poor stability in the reaction medium under oxidizing conditions, and are rapidly deactivated [9,10]. Catalytic reactions in homogeneous phase have from a practical point of view some disadvantages, such as the catalyst deactivation and the lack of recycling methods, which make difficult their application in large scale processes. Several

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researchers have been involved in the heterogenization of metal porphyrins and phthalocyanines, encapsulating the complexes in zeolites [11–13], supporting them on polymers [14,15] or by intercalation in layered solids like clays [16] and zirconium phosphate [17,18].

In the present work, metal phthalocyanines (MPc) and metal tetraphenylporphyrins (MPr) were intercalated in α-zirconium hydrogen phosphate: α-$Zr(HPO_4)\cdot H_2O$, (α-ZrP), a lamellar solid acid with high cationic exchange capacity [19]. We have investigated the epoxidation of olefins by $O_2$ in presence of isobutyraldehyde [20], using free metal complexes in solution and intercalated in α-zirconium phosphate (α-ZrP-M, α-ZrP-MPc and α-ZrP-MPr, M: Mn, Fe, Co). Free MPc and MPr in solution in our reaction conditions are quickly degraded within 1 h of reaction, while the intercalated complexes are protected by the matrix α-ZrP.

In order to verify if acylperoxy radicals or peroxy acids are the oxidizing agents, we tested the oxidation of *cis*-stilbene. We have observed that cyclohexene was oxidized by dioxygen plus isobutyraldehyde with high yields of epoxide, some allylic oxidation products with the concomitant co-oxidation of the isobutyraldehyde to the corresponding carboxylic acid. The yield of products depends on the metal and the ligand type intercalated in α-ZrP. The presence of free radicals was confirmed by addition of a free radical quencher *N*-phenyl-1-naphthylamine, which inhibited the reaction [21]. Different ratios of *cis*- to *trans*-stilbene oxide obtained suggest that there is another oxidizing agent in addition to free radicals, perhaps a metal oxo intermediate.

## 2. Experimental

The α-ZrP matrix was prepared and then exchanged with different metals (α-ZrP-M, M: Mn, Fe, Co and Na), it was also exchanged with imidazol (α-ZrP-Imi). The complexes MPc and MPr were intercalated in α-ZrP by two methods. Method A was used for the intercalation of metallophthalocyanines α-ZrP-MPc and method B for the intercalation of metalloporphyrins α-ZrP-MPr. The free and intercalated complexes were characterized and tested in the oxidation of cyclohexene. *Cis*-stilbene was oxidized with intercalated complex plus dioxygen and isobutyraldehyde. Control reactions were carried out to determine the substrate:isobutyraldehyde ratio at which no reaction takes place without the catalyst. A radical quencher, *N*-phenyl-1-naphthylamine was added to the reactions in order to verify if a free radical mechanism is present. The oxidation of *cis*-stilbene in presence of isobutyraldehyde plus dioxygen in absence of the catalyst or in presence of 3-chloroperbenzoic acid was tested in order to verify if acylperoxy radicals or peroxy acid are the oxidizing agents.

### 2.1. Instrumentation

X-ray diffraction patterns of oriented samples of α-ZrP-M, α-ZrP-MPc and α-ZrP-MPr were collected at room temperature from 2 to 70° in $2\theta$, using a D-MAX IIIB Rigaku system. The diffractometer was operated at 40 kV and 80 mA and the Cu Kα radiation was selected using a graphite monochromator. Infrared spectra were taken in a Perkin Elmer model 1750 FT-IR. Thermogravimetric analysis were carried out on a TA Instrument 2000 Thermal Analyzer under $N_2$ flow (10°C/min, from 298 up to 973 K). Metallophthalocyanines and metalloporphyrins were analyzed by UV–VIS spectroscopy in a Hewlett-Packard 8453. The amount of metal exchanged in the α-ZrP-M was determined by atomic absorption spectroscopy in a Perkin Elmer model 372. The intercalated MPr in α-ZrP was quantified measuring the amount of metal after destroying the matrix with a mixture of 1:1 v/v of HF (45%) and HCl (35%). The metal was quantified by atomic absorption spectroscopy in a Perkin Elmer model 372. The intercalated MPc in α-ZrP was determined by dissolving the sample in concentrated $H_2SO_4$ and measuring the complex absorption bands by UV–VIS spectroscopy; the concentration of MPc was calculated from a calibration curve, the standards were prepared dissolving known amounts of free MPc in $H_2SO_4$ and adding α-ZrP to take into account the matrix effects.

### 2.2. Materials

All compounds employed were of reagent grade and used without further purification. Zirconium(IV) oxide chloride octahydrate, manganese acetate tetrahydrate ($Mn(CH_3COO)_2\cdot 4H_2O$), iron sulfate heptahydrate ($FeSO_4\cdot 7H_2O$), cobalt acetate tetrahydrate ($Co(CH_3COO)_2\cdot 4H_2O$), imidazol, 3-chloroperbenzoic acid,

isobutyraldehyde, acetone, ethanol, hydrofluoric acid and cyclohexene were purchased from Merck. 1,2-Dicyanobenzene, iron, manganese and cobalt phthalocyanines (FePc, MnPc and CoPc) were obtained from Acros. Dichloromethane, phosphoric acid, sulfuric acid, dioxane and toluene were purchased from JT Backer. *Cis*-stilbene, *N*-phenyl-1-naphthylamine, pyrrol and benzaldehyde were purchased from Aldrich. Ferric chloride ($FeCl_3 \cdot 6H_2O$), *N*,*N*-dimethylformamide and methanol were obtained from Carlo Erba.

### 2.3. Preparations

#### 2.3.1. Tetraphenylporphyrin

The tetraphenylporphyrin [$H_2TPP$] was synthesized mixing 350 ml of propionic acid, 8 ml of pyrrol and 12 ml of benzaldehyde in a flask and refluxing about 0.5 h. The [$H_2TPP$] crystal formed were separated from the solution by filtration and washed with deionized water and methanol [22].

#### 2.3.2. Iron tetraphenylporphyrin

The Fe(TPPCl) was prepared by dissolving $3.3 \times 10^{-4}$ mol of [$H_2TPP$] and $3.9 \times 10^{-4}$ mol of $FeCl_3 \cdot 6H_2O$ in 50 ml of *N*,*N*-dimethylformamide in a flask and refluxing about 6 h. The solution was cooled in an ice bath and then 50 ml of saturated saline solution was added. The Fe(TPPCl) crystal formed were separated from the solution by filtration and washed with deionized water and methanol [23].

#### 2.3.3. Cobalt tetraphenylporphyrin

The cobalt(II) tetraphenylporphyrin, (CoTPP), was prepared mixing $3.2 \times 10^{-4}$ mol of tetraphenylporphyrin in 50 ml of dioxane, $3.5 \times 10^{-4}$ mol of cobalt acetate and 1.5 ml of acetic acid in a flask and refluxing it during 7 h. The solution was cooled to room temperature, and then 50 ml of deionized water was added. The CoTPP crystal formed were separated from the solution by filtration and washed with deionized water and methanol [24].

#### 2.3.4. α-Zirconium phosphate

The α-zirconium phosphate, α-$Zr(HPO_4) \cdot H_2O$ (α-ZrP), was synthesized dissolving 33 g of $ZrOCl_2 \cdot 8H_2O$ in 510 ml deionized water, then 38 ml of 40% hydrofluoric acid and 276 ml of 85% phosphoric acid were added while the solution was stirred, then the mixture was set under reflux during 15 days. The solid obtained was filtered and washed with 2 M phosphoric acid and then with deionized water until the filtrate was free of chloride ion and then dried during 24 h at 383 K [25].

#### 2.3.5. Exchange of imidazol in α-ZrP

In order to exchange the metal complex into α-ZrP, it is necessary to increase the interlayer space exchanging imidazol. The α-ZrP-Imi was prepared dissolving in water 0.005 mmol of imidazol per gram of α-ZrP, the mixture was stirred under reflux during 4 days.

#### 2.3.6. Exchange of metals in α-ZrP

The α-ZrP-M (M: Mn, Fe, Co) were prepared dissolving 0.013 mol of manganese acetate tetrahydrate, iron sulfate heptahydrate or cobalt acetate, in 100 ml of 0.1 M NaCl and NaOH, 4 g of α-ZrP was added, the mixture was set under reflux during 24 h. The α-ZrP-Na was prepared mixing a solution 0.2 M of NaCl and 0.1 M of NaOH with 5 g of α-ZrP, the mixture was set under reflux during 6 h. The solids obtained were filtered and washed with deionized water until the filtrate was free of chloride ion and then dried during 24 h at 383 K [26]. The α-ZrP-Mn and α-ZrP-Na were obtained as a white solid, the α-ZrP-Fe as a yellow solid, α-ZrP-Co as a blue solid.

#### 2.3.7. Synthesis "in situ" of phthalocyanines in α-ZrP (method A)

The α-ZrP-MPc (MPc: CoPc, FePc, MnPc) were synthesized "in situ" by formation of MPc inside of α-ZrP. A mixture of $6 \times 10^{-3}$ mol of the metal exchanged α-ZrP-M with 0.05 mol of 1,2-dicyanobenzene were introduced in a glass ampoule, air was evacuated ($10^{-4}$ mmHg) and the recipient sealed and heated in an oven at 473 K for 24 h. The products of the reaction were purified by successive Soxhlet extraction with different solvents: acetone (3 days), methanol (2 days), and dichloromethane (2 days). The α-ZrP-CoPc was obtained as a blue solid, the α-ZrP-MnPc as a gray solid and the α-ZrP-FePc as a brown solid. The solids were dried during 1 h at 383 K.

#### 2.3.8. Exchange of tetraphenylporphyrins in α-ZrP (method B)

In order to intercalate the metal porphyrins it was necessary to expand the basal spacing of α-ZrP

Table 1
Characteristic absorption bands of metal complexes

| Metal complex | Q band | B or Soret band | Solvent |
|---|---|---|---|
| CoPc | 784 | 424 | $H_2SO_4$ |
| FePc | 780 | 450 | $H_2SO_4$ |
| MnPc | 837 | 425 | $H_2SO_4$ |
| Fe(TPPCl) | 575 | 417 | DMF |
| CoTPP | 528 | 410 | $CH_2Cl_2$ |

with imidazol or sodium. Due to the larger size of Fe(TPPCl) it was intercalated in α-ZrP-Imi which presents a wider spacing and the CoTPP was intercalated in α-ZrP-Na. An amount of 1 g of α-ZrP-Imi was slowly added to a solution of Fe(TPPCl) (0.03 mmol) in 50 ml of ethanol and the resulting suspension was stirred under reflux during 4 days. The brown solid was filtered, washed with methanol and dried at 383 K.

An amount of 1 g of α-ZrP-Na was slowly added to a solution of CoTPP (0.05 mmol) in 50 ml of ethanol. The suspension was heated under reflux during 4 days. The pink solid was filtered, washed with methanol and dried at 383 K [27].

*2.3.9. Characterization of the metal complexes*

Free metallophthalocyanines and metalloporphyrins were characterized by UV–VIS spectroscopy, the results are given in Table 1. We confirmed the presence of the metal complexes principally by Q and Soret bands that indicate ($\pi$, $\pi^*$) transitions [28].

*2.3.10. Characterization of α-ZrP-M, α-ZrP-MPc and α-ZrP-MPr*

*2.3.10.1. Atomic absorption.* The amount of metal exchanged per gram of α-ZrP-M was $1.6 \times 10^{-3}$, $2.3 \times 10^{-3}$, and $1.6 \times 10^{-3}$ mol of Mn, Fe and Co, respectively. The intercalated porphyrin was $0.3 \times 10^{-4}$ mmol of Fe(TPPCl) per gram of α-ZrP-Imi-Fe(TPPCl) and $0.2 \times 10^{-6}$ mol CoTPP per gram of α-ZrP-CoTPP.

*2.3.10.2. UV–VIS spectroscopy.* The amounts of MPc present per gram of α-ZrP were found to be $0.4 \times 10^{-3}$, $0.2 \times 10^{-3}$ and $0.5 \times 10^{-3}$ mol of MnPc, FePc and CoPc, respectively.

*2.3.10.3. Powder X-ray diffraction (XRD).* Fig. 1 shows the diffraction profile of α-ZrP, α-ZrP-Co, α-ZrP-CoPc fresh and after 24 h of reaction. The basal spacing of the most intense reflection corresponding to the (0 0 2) plane of α-ZrP [29] presents a shift in the intercalated complexes. The spacing of the fresh and used catalysts are given in Table 2. The basal spacing of the greatest intense reflection corresponding to the (0 0 2) plane for the α-ZrP is 7.58 Å, after the metal

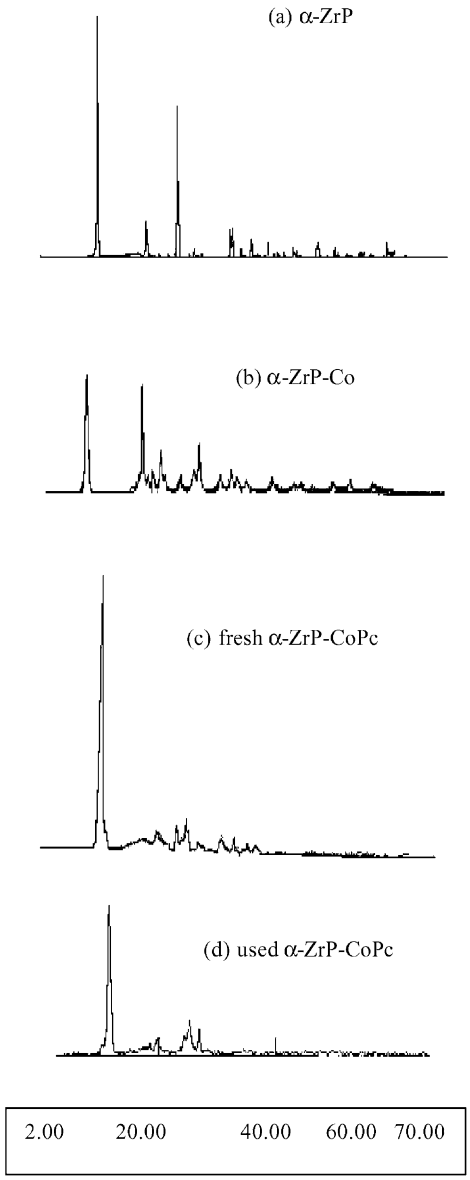



Fig. 1. Powder X-ray diffraction of (a) α-ZrP; (b) α-ZrP-Co; (c) fresh α-ZrP-CoPc; (d) used α-ZrP-CoPc.

Table 2
Spacing corresponding to the plane (0 0 2) in the catalytic systems α-ZrP-M, α-ZrP-MPc and α-ZrP-MPr

| Catalyst (fresh) | $d_{002}$ (Å) | Catalyst (fresh) | $d_{002}$ (Å) | Catalyst (used) | $d_{002}$ (Å) |
|---|---|---|---|---|---|
| α-ZrP | 7.58 | | | | |
| α-ZrP-Na | 8.4 | α-ZrP-Na-CoTPP | 8.45 | α-ZrP-Na-CoTPP | 8.45 |
| α-ZrP-Imi | 10.7 | α-ZrP-Imi-Fe(TPPCl) | 10.8 | α-ZrP-Imi-Fe(TPPCl) | 10.8 |
| α-ZrP-Co | 9.6 | α-ZrP-CoPc | 8.23 | α-ZrP-CoPc | 8.20 |
| α-ZrP-Fe | 7.53 | α-ZrP-FePc | 7.49 | α-ZrP-FePc | 7.49 |
| α-ZrP-Mn | 9.75 | α-ZrP-MnPc | 8.06 | α-ZrP-MnPc | 8.1 |

exchange procedure this value increased and when the complex was intercalated the corresponding value decreased (Table 2). XRD analysis show that the metal complex intercalated was retained in the used catalyst (Fig. 1).

*2.3.10.4. FT-IR spectroscopy.* FT-IR spectra of α-ZrP, α-ZrP-Co and α-ZrP-CoPc fresh and after 24 h of reaction are shown in Fig. 2. The water of crystallization and the phosphate group of α-ZrP has been studied by IR spectroscopy, three characteristic bands are present in the OH stretching region, the results are in full agreement with those reported earlier [30]. The α-ZrP-Co spectrum present a narrow band due to the phosphate group around 1000 $cm^{-1}$. The presence of MnPc and FePc in the α-ZrP were confirmed by the bands between 1250 and 1550 $cm^{-1}$ attributed to C–C stretching vibrations of the phenyl or isoindole rings. In the α-ZrP-Imi-Fe(TPPCl) the C–H stretching of the pyrrolic ring at 1458 $cm^{-1}$ was observed. The α-ZrP-Na-CoTPP presents an additional band at 1385 $cm^{-1}$ (=C–N strain).

*2.3.10.5. Thermogravimetric analysis.* A 5.9% weight loss is observed in α-ZrP between 405 and 432 K, corresponding to the loss of 1 mol of water of crystallization and another equivalent loss between 714 and 781 K caused by the loss of 1 mol of structural water, due to the condensation of phosphate groups [31]. The α-ZrP-CoPc loss of 6.8% between 683 and 851 K due to the decomposition of the CoPc was in agreement with the decomposition temperature observed for the complex.

*2.3.11. Catalytic test*

All the catalytic tests were performed in a 50 ml microreactor, Parr 4592, with stirring at 300 K and under 100 Pa of oxygen relative pressure. Gas chromatography (GC) analysis of the reactants and the products of the reaction were performed with a Hewlett-Packard HP6890 chromatograph equipped with a flame ionization detector and silica capillary column HP-5 (crosslinked 5% PhMeSiloxane, 30 m × 0.32 mm × 0.25 μm) with He as carrier gas. Toluene was used as internal standard for the GC analysis.

*2.3.12. Oxidation of cyclohexene*

In the homogeneous reactions $1 \times 10^{-5}$ mol of free metal complexes (MPc, MPr) were dissolved in 0.331 mol dichloromethane, then were added 0.01 mol of cyclohexene, 0.01 mol of isobutyraldehyde and $2.7 \times 10^{-3}$ mol of toluene (internal standard).

In the heterogeneous reactions an amount of intercalated complex (α-ZrP-MPc, α-ZrP-MPr) containing $1 \times 10^{-4}$ mol of complex were added in 0.331 mol dichloromethane, 0.01 mol of cyclohexene, 0.01 mol of isobutyraldehyde and $2.7 \times 10^{-3}$ mol of toluene (internal standard).

*2.3.13. Oxidation of cis-stilbene*

The reaction mixture contains $4 \times 10^{-3}$ mol of *cis*-stilbene, $8.8 \times 10^{-3}$ mol of isobutyraldehyde, 0.27 md of dichloromethane, $2.7 \times 10^{-3}$ mol of toluene (internal standard) and an amount of intercalated complex (α-ZrP-MPc, α-ZrP-MPr) containing $1 \times 10^{-4}$ mol of complex. With α-ZrP-MPr the reaction mixture contained $13.5 \times 10^{-3}$ mol of isobutyraldehyde, in this case with lower concentrations of isobutyraldehyde the reaction did not proceed.

*2.3.14. Control reactions*

Since there is some oxidation of cyclohexene with isobutyraldehyde in absence of the catalyst, control reactions were carried out to determine the

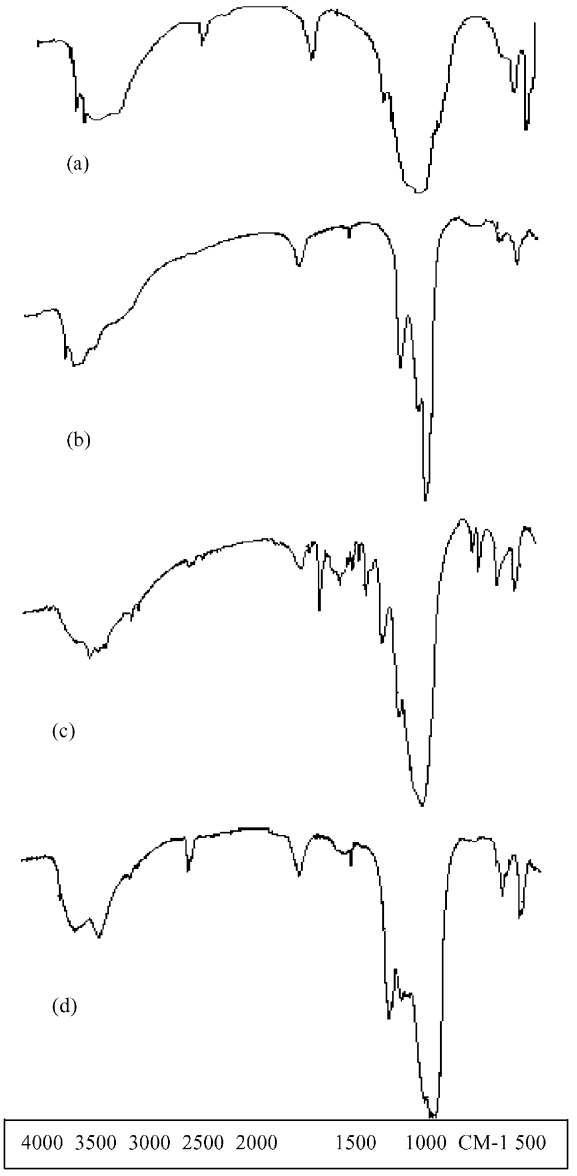



Fig. 2. FT-IR spectra of (a) α-ZrP; (b) α-ZrP-Co; (c) fresh α-ZrP-CoPc; (d) used α-ZrP-CoPc.

cyclohexene:isobutyraldehyde ratio at which no reaction takes place without the catalyst. We have also studied the epoxidation of cyclohexene in presence and absence of dioxygen in order to verify its effect in the reaction. A radical quencher, *N*-phenyl-1-naphthylamine ($1.4 \times 10^{-4}$ mol), was added to the reactions with CoPc and α-ZrP-CoPc in order to verify if a free radical mechanism is present.

The *cis*-stilbene oxidation was tested to determine the *cis*-stilbene:isobutyraldehyde ratio at which no reaction takes place without the catalyst, also since the stereoselectivity of *cis*-stilbene oxidation depends on the oxidation pathway, it was studied in absence of the catalyst and in presence of peracid, the reaction contains $4 \times 10^{-3}$ mol of *cis*-stilbene with $8 \times 10^{-3}$ mol of 3-cloroperbenzoic acid (MPCBA) in 0.27 mol of dichloromethane, $2.7 \times 10^{-3}$ mol of toluene (internal standard) and $1 \times 10^{-4}$ mol of intercalated complex in α-ZrP.

## 3. Results and discussion

### 3.1. Control reactions

The control reactions allow to see the effect of each one of the components of the reaction: cyclohexene does not react when it is in contact with the solvent and oxygen alone during 24 h. Cyclohexene does not suffer any transformation when the reaction is carried out with α-ZrP as the catalyst. The reaction proceeded without catalyst when a ratio 1:2 or higher of cyclohexene:isobutyraldehyde was used and a 2.5% yield of epoxide was obtained after 1 h of reaction. When a ratio 1:1 of cyclohexene:isobutyraldehyde was used the reaction does not proceed without the catalyst. Isobutyraldehyde is oxidized to 2-methylpropionic acid in presence of cyclohexene and *cis*-stilbene, the MPc, MPr, α-ZrP-M, α-ZrP-MPr or α-ZrP-MPc and dioxygen.

When either dioxygen, MPc, MPr, α-ZrP-M, α-ZrP-MPr, α-ZrP-MPc or isobutyraldehyde are absent in the reaction medium or when cyclohexene:isobutyraldehyde ratio is equal or lower that 1:1, there is no conversion of cyclohexene. The reaction does not proceed when a free radical inhibitor is added at the beginning of the reaction. Addition of the free radical inhibitor at any time stopped the reaction, suggesting that free radicals are playing an important role.

### 3.2. Oxidation of cyclohexene with free complexes

Table 3 presents the yield of epoxide obtained with metal complexes in solution at 18% cyclohexene

Table 3
Epoxidation of cyclohexene by $O_2$ plus isobutyraldehyde in the presence of the free metalloporphyrins and metallophthalocyanines[a]

| Catalyst | Epoxide yield[b] (%) | Epoxide/ alillic[c] | Reaction time (h) |
|---|---|---|---|
| CoPc | 12.5 | 7.0 | 0.8 |
| FePc | 31.8 | 4.0 | 0.7 |
| MnPc | 25.1 | 3.0 | 0.8 |
| CoTPP | 0.0 | – | – |
| Fe(TPPCl) | 18.4 | 4.0 | 0.8 |

[a] Reaction conditions: MPc or MPr ($1 \times 10^{-5}$ mol), cyclohexene (0.01 mol) and isobutyraldehyde (0.01 mol) in $CH_2Cl_2$ (0.331 mol) under 100 Pa oxygen relative pressure and 300 K.

[b] Yield (%), mole epoxide/initial mole cyclohexene at 18% cyclohexene total conversion. Total conversion (%) (mole cyclohexene at time/mole converted cyclohexene).

[c] Epoxide/allylic products ratio, mole epoxide/mole (cyclohexenol + cyclohexenone).

total conversion. Oxidation of cyclohexene with metalloporphyrins or metallophthalocyanines gave cyclohexene oxide as the predominant product and some allylic oxidation products, cyclohexenol and cyclohexenone, as minor products. The product distributions were different for each metal complex. Metallophthalocyanines are more actives than metalloporphyrins. A higher yield of epoxide were obtained with FePc.

### 3.3. Oxidation of cyclohexene with intercalated complexes

The results of oxidation of cyclohexene with α-ZrP-M, α-ZrP-MPc and α-ZrP-MPr at 15% cyclohexene total conversion are summarized in Table 4. With α-ZrP-M (M: Mn, Fe, Co), α-ZrP-Imi-Fe(TPPCl) and α-ZrP-Na-CoTPP only epoxide is obtained. In α-ZrP-MPc the epoxide is the predominant product while allylic oxidation products were obtained in smaller proportion. The intercalated complexes in α-ZrP show more activity than α-ZrP-M, and the α-ZrP-MPc are more active than the α-ZrP-MPr. The highest yield of cyclohexene oxide is obtained with α-ZrP-FePc. The product distributions depend on the individual intercalated complex.

### 3.4. Oxidation of cis-stilbene with intercalated complexes

The oxidation of *cis*-stilbene were carried out using the intercalated complexes. The yield for each product obtained with α-ZrP-MPc and α-ZrP-FePr at 15% *cis*-stilbene total conversion, are given in Table 5. *Cis*-stilbene was oxidized to a mixture of *cis*- and *trans*-stilbene oxide and benzaldehyde. There is a variation in the *cis*- to *trans*-stilbene oxide ratio and in benzaldehyde yield, depending of the catalyst used.

Table 4
Results of the oxidation of cyclohexene with dioxygen plus isobutyraldehyde in the presence of α-ZrP-MPc and α-ZrP-MPr[a]

| Catalyst | Epoxide yield[b] (%) | Epoxide/alillic[c] | Reaction time (h) |
|---|---|---|---|
| α-ZrP | 0.0 | – | – |
| α-ZrP-Na | 4.2[d] | – | 5.0 |
| α-ZrP-Imi | 4.3[d] | – | 5.0 |
| α-ZrP-Co | 7.5 | – | 1.0 |
| α-ZrP-Fe | 4.9 | – | 1.0 |
| α-ZrP-Mn | 4.1 | – | 1.0 |
| α-ZrP-MnPc | 15.21 | 10 | 0.3 |
| α-ZrP-FePc | 31.18 | 23 | 0.3 |
| α-ZrP-CoPc | 20.0 | 20 | 0.3 |
| α-ZrP-Imi-Fe(TPPCl) | 10.77 | – | 4.0 |
| α-ZrP-Na-CoTPP | 11.1 | – | 1.0 |

[a] Reaction conditions: α-ZrP-MPc, α-ZrP-MPr ($1 \times 10^{-4}$ mol of intercalated complex), cyclohexene (0.01 mol) and isobutyraldehyde (0.01 mol) in $CH_2Cl_2$ (0.331 mol). Under 100 Pa oxygen relative pressure and 300 K.

[b] Yield (%), mole epoxide/initial mole cyclohexene at 15% cyclohexene total conversion.

[c] Epoxide/allylic products ratio, mole epoxide/mole (cyclohexenol + cyclohexenone).

[d] At 2.5% cyclohexene total conversion.

Table 5
Oxidation of *cis*-stilbene by $O_2$ plus isobutyraldehyde in presence of intercalated complexes[a]

| Catalyst | Reaction time (h) | Yield[b] (%) | | | *Cis/trans*-oxide ratio[c] |
|---|---|---|---|---|---|
| | | *Cis*-stilbene oxide | *Trans*-stilbene oxide | Benzaldehyde | |
| α-ZrP-MnPc | 0.8 | 11.0 | 18.4 | 1.7 | 0.7 |
| α-ZrP-FePc | 0.6 | 33.5 | 39.0 | 6.1 | 0.9 |
| α-ZrP-CoPc | 0.7 | 12.2 | 23.2 | 7.1 | 0.5 |
| α-ZrP-Imi-Fe(TPPCl) | 2.0 | 2.8 | 1.3 | 0.0 | 2.0 |

[a] Reaction conditions: α-ZrP-MPc ($1 \times 10^{-4}$ mol of intercalated complex), *cis*-stilbene ($4 \times 10^{-3}$ mol) and isobutyraldehyde ($8.8 \times 10^{-3}$ mol) in dichloromethane (0.27 mol). α-ZrP-MPr ($4 \times 10^{-5}$ mol of intercalated complex), *cis*-stilbene ($4 \times 10^{-3}$ mol) and isobutyraldehyde ($13.5 \times 10^{-3}$ mol) in dichloromethane (0.27 mol). Under 100 Pa oxygen relative pressure.
[b] Yield (%), mole product/initial mole *cis*-stilbene at 15% *cis*-stilbene total conversion.
[c] *Cis/trans*-stilbene oxide ratio, mole *cis*-stilbene oxide/mole *trans*-stilbene oxide.

The highest yields of *cis*-stilbene oxide were obtained with α-ZrP-FePc.

### 3.5. Stability of free complexes

The behavior of the free complexes in the reaction medium was followed by UV–VIS spectroscopy. CoTPP and CoPc UV–VIS spectra are shown in Figs. 3 and 4, respectively. Degradation of the complexes is evident, in agreement with other authors who have observed the deactivation of metalloporphyrins and metallophthalocyanines with oxidants such as, hydrogen peroxide, organic peroxides or iodosylbenzene [32,33]. In the cases of MnPc, FePc and Fe(TPPCl) the disappearance of the bands is observed after 30 min of reaction. Phthalocyanines have a very poor stability and are rapidly deactivated when used as catalysts in hydrocarbon oxidation [34]. This phenomenon has been discussed in the literature and different hypotheses have been put forward to explain it. Some authors believe that phthalocyanine is degraded into small soluble fragments [35]. The reactions in homogeneous phase gave mainly cyclohexene oxide, even though the complex is destroyed within few minutes, some activity remains, due perhaps to soluble metallic fragments formed from the

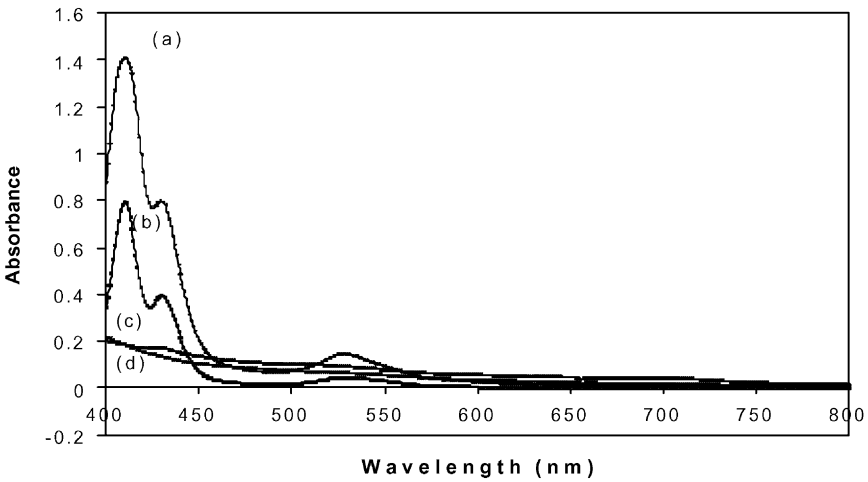



Fig. 3. Degradation of CoTPP during oxidation of cyclohexene with $O_2$ plus isobutyraldehyde in dichloromethane at different reaction times: (a) 0 min; (b) 1 h; (c) 2 h; (d) 4 h.

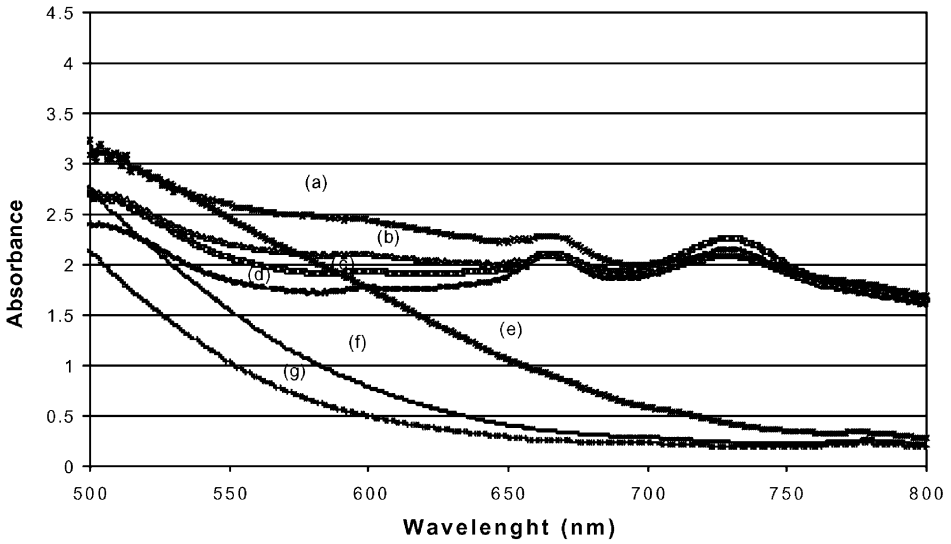



Fig. 4. Degradation of the CoPc with $O_2$ plus isobutyraldehyde in dichloromethane at different reaction times: (a) 0 min; (b) 1 min; (c) 5 min; (d) 15 min; (e) 30 min; (d) 45 min; (e) 1 h; (f) 2 h; (g) 4 h.

destruction of the complex. It is important to note that the complex is absolutely necessary to produce the catalytic activity when a ratio equal or greater than 1:1 of cyclohexene:isobutyraldehyde is used.

### 3.6. Stability of intercalated complexes

Fig. 5 shows the UV–VIS absorption spectra of α-ZrP-CoPc dissolved in sulfuric acid, of fresh and used catalyst. All intercalated complexes (α-ZrP-MPc,

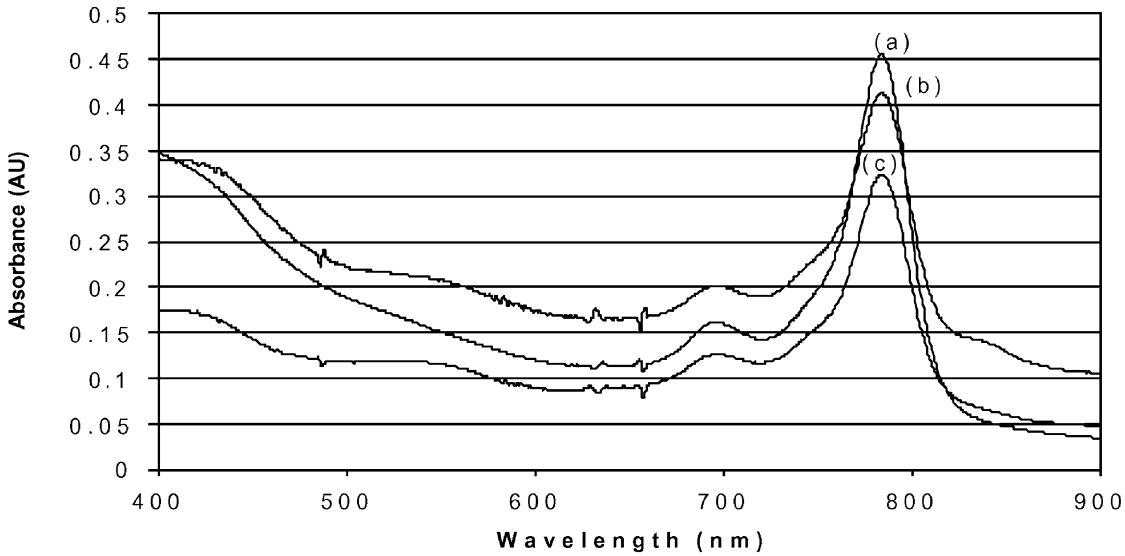



Fig. 5. The UV–VIS absorption spectra in concentrated sulfuric acid of CoPc in α-ZrP-CoPc (a) fresh, (b) used once, and (c) used twice after 24 h of reaction.

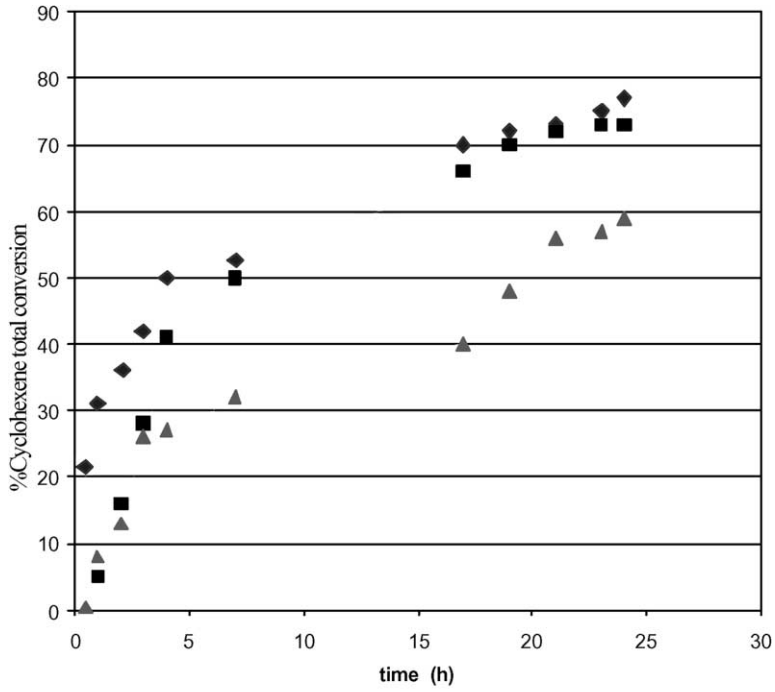



Fig. 6. Percent cyclohexene total conversion with α-ZrP-CoPc (◆) fresh, (■) used once after 24 h of reaction, and (▲) used twice after 24 h of reaction.

α-ZrP-MPr) show the characteristic absorption bands of the free complexes in concentrated $H_2SO_4$.

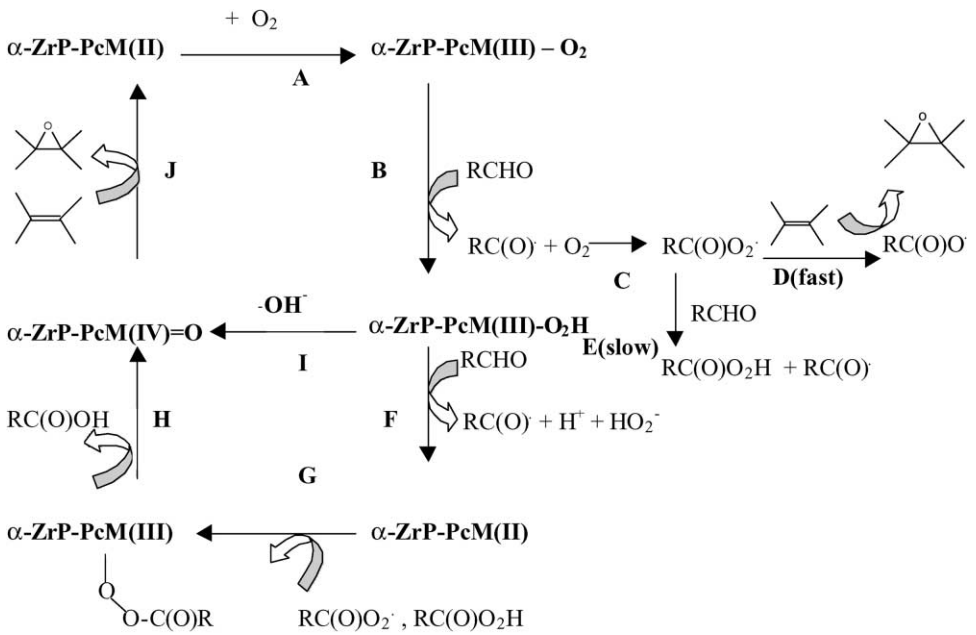
Fig. 6 presents the cyclohexene total conversion with fresh and used α-ZrP-CoPc. Catalytic activity of the intercalated complexes is preserved after 24 h of reaction. These results show that the matrix protects the metal complex, CoPc.

### 3.7. Mechanistic considerations

We have studied oxidation reactions with dioxygen plus aldehyde in homogeneous and heterogeneous phase, under catalytic conditions, using 1:1 cyclohexene-isobutyraldehyde ratio in which no reaction take place without the catalyst. A tentative mechanism proposed for the intercalated complexes-catalyzed oxygenation of substrates by $O_2$ and aldehydes is given in Scheme 1. We assumed that oxygenation of the substrate to occur either via radicals (acyl and acylperoxy) or reactive high-valent metal oxo intermediates, which are produced by the reaction of the peroxyacid with the metal catalysts and which then react with the olefin in a fashion analogous to that observed previously for metal complex-catalyzed reactions of peroxy acids with olefins [36,37].

Usually, species such as metal–iodosylbenzene complexes and metal–OOR complexes (R: H, $CR'_3$, $C(O)R'$), are the precursors of high-valent metal oxo complexes ($L_nM{=}O$, $L_n$: ligand, M: metal) [38,39]. Oxygenation of substrate is assumed to occur via reactive high-valent metal oxo intermediates. Groves et al. [40] were the first to prepare and characterize a high-valent iron(IV) oxo porphyrin cation radical complex, $(TMP)^{\bullet+}Fe(IV){=}O$ (TMP: meso-tetramesitylporphyrin). Since then, a number of high-valent iron(IV) oxo porphyrin cation radical complexes have been prepared (at low temperature) and well characterized with a variety of spectroscopic methods such as UV–VIS, EPR, Mossbauer, EXAFS, NMR, Raman, and magnetic circular dichroism [41].

The metal complexes may play an important role in the initiation step: the transition metal probably binds




Scheme 1. Catalytic cycle proposed for olefins oxidation with dioxygen plus isobutyraldehyde in presence of heterogeneous catalysts α-ZrP-MPc or α-ZrP-MPr (M: Mn, Fe, Co; Pc: phthalocyanine; Pr: porphyrin).

to $O_2$ to form a dioxygen complex α-ZrP-MPc-$O_2$ or α-ZrP-MPr-$O_2$, pathway A [42,43]. If dioxygen complexes are formed, then the degree of reversibility of binding $O_2$ to the metal complex depends very strongly on the metal and on the ligand. In our reaction conditions we have observed a catalytic effect with homogeneous and heterogeneous catalysts, which depends on the metal complex.

The catalysts MPr, MPc, α-ZrP-MPr or α-ZrP-MPc, may bind $O_2$ to form species which have sufficient radical character to abstract a hydrogen atom from an aldehyde to yield an acyl radical ($(CH_3)_2CHC(O)^{\bullet}$), pathway B. The presence of free radicals was confirmed by addition of a free radical quencher, which inhibited the reaction, indicating that a free radical chain mechanism is taking place. The acyl radical could react with dioxygen to give an acylperoxy radical ($(CH_3)_2CHC(O)O_2^{\bullet}$), which acts as a carrier in a chain mechanism, pathway C.

The acylperoxy radical may react with both isobutyraldehyde, pathway E or olefins, pathway D to produce a peroxy acid ($(CH_3)_2CHC(O)O_2H$) or to give epoxide. The acylperoxy radical has a greater tendency to yield epoxides by addition to the double bond of olefins rather than to abstract an allylic hydrogen atom of the olefins to give allylic oxidation products, whereas hydroxyl and alkylperoxy radicals tend to abstract an allylic hydrogen [44]. It has been previously shown that the acylperoxy radical generated in the reaction is a competent oxidizing agent for olefins epoxidation [45]. The role of α-ZrP-MPr or α-ZrP-MPc could be either to increase the velocity of formation of acyl and acylperoxy radicals or to form a high-valent metal oxo complex.

In order to verify if the acylperoxy radicals or peroxy acids are the oxidizing agents, we have examined the oxidation of *cis*-stilbene. It has been reported that the acylperoxy radical oxidize *cis*-stilbene to *trans*-stilbene oxide [20,46], while that the reaction of *cis*-stilbene with peroxy acids forms stereoselectively *cis*-stilbene oxide [47]. We have found that *trans*-stilbene oxide was produced during the oxidation of *cis*-stilbene with oxygen plus isobutyraldehyde in absence of the catalyst while the reaction of *cis*-stilbene with 3-cloroperbenzoic acid without catalyst forms stereoselectively *cis*-stilbene oxide. Therefore, we may conclude that the epoxidizing intermediate is not the peroxy acid, presumably be-

cause the rate of the reaction of the acylperoxy radical with *cis*-stilbene is faster than that of its reaction with aldehyde. This could suggest that pathway D is faster than pathway E. In our reaction conditions, during the oxidation of *cis*-stilbene with catalyst, we have obtained benzaldehyde and a different ratio of *cis* to *trans* for each catalytic system (Table 5), this could indicate the participation of an acylperoxy radical, which favors the formation of *trans*-stilbene oxide. But the different ratios *cis*- to *trans*-stilbene oxide obtained suggest that besides the free radicals perhaps the metal oxo intermediate is responsible for some fractions of the oxidation of olefins in this system.

The reaction of the acylperoxy radical or peroxy acid with the α-ZrP-MPc or α-ZrP-MPr could form a metal-peroxy complex, (α-ZrP-MPc–O–O–C(O)–CH $(CH_3)_2$), pathway G. The heterolytic O–O bond cleavage in the metal-peroxy complex, pathway H, may lead to the formation of the high-valent metal oxo complex (α-ZrP-PcM=O). The hydroperoxide complex (α-ZrP-MPc-$O_2$H) produced in the pathway B, could also form the high-valent metal oxo complex by heterolytic O–O bond cleavage, pathway I. It has often been assumed that high-valent metal oxo species are the most likely active intermediates when olefins are selectively oxidized to the corresponding epoxides in oxygen atom transfer reactions, pathway I. The selectivity of the reaction *cis*-stilbene oxidation is affected by the formation of a metal oxo complex. The α-ZrP-Imi-Fe(TPPCl) present retention of the configuration during the epoxidation of *cis*-stilbene, while α-ZrP-MPc present a low retention of the configuration, it has been suggested that the carbocation intermediate could be partially stabilized by the electron density on porphyrin nitrogens [1,47].

## 4. Conclusions

- Free MPc and MPr complexes in our reaction conditions are quickly degraded within 1 h of reaction, while with the intercalated complexes, the metallophthalocyanines are protected by α-ZrP and show activity even after 24 h of reaction.
- The selectivity during oxidation of cyclohexene and *cis*-stilbene with dioxygen plus isobutyraldehyde in presence of α-ZrP-M, α-ZrP-MPc and α-ZrP-MPr depends on the metal complex intercalated.
- A free radical mechanism must be present in this type of reaction.

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