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Journal of Molecular Catalysis A: Chemical 152 (2000) 111–115

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Pernitrated metalloporphyrins as catalysts in oxidation with magnesium monoperoxophthalate
I. Epoxidation of cyclic olefins

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Received 12 January 1999; accepted 16 June 1999

Abstract

Metalloporphyrins with several nitro groups in β-positions were used in the epoxidation of cyclic olefins with magnesium monoperoxyphthalate (MMPP) as an oxygen atom donor, under mild conditions. Iron- and manganese-pernitrated complexes are able to promote the epoxidation of alkenes without requiring the addition of any nitrogen base. Cobalt porphyrins showed low activity, but addition of the cocatalyst raised it.

Keywords: Metalloporphyrins; Cyclic olefins; Epoxidation

1. Introduction

Mimicking the ability of cytochrome *P*-450 to oxidize organic substrates by synthetic metalloporphyrins as catalysts is well-documented in the literature [1,2]. However, most systems require the addition of a cocatalyst which acts as an axial ligand ''proximal effect'' and remarkably improves the rate as well as chemo- and stereoselectivity of the reaction [3–5]. A variety of metalloporphyrins have been tested, among them complexes carrying substituents on the β-pyrrole position — third-generation porphyrins which show an exceptionally high catalytic efficiency and resistance to attack by strong oxidizing agents [6–8]. Little is known, however, about catalytic properties of metalloporphyrins carrying $-NO_2$ on the β-pyrrole positions. We have therefore undertaken investigations aimed at the synthesis of such metalloporphyrins and their application in oxidation of hydrocarbons using single oxygen donors. Some time ago, we have shown that halogenated and perhalogenated metalloporphyrins are active catalysts for the epoxidation of propene and the hydroxylation of cyclohexane with magnesium monoperoxyphthalate (MMPP) as an oxygen donor [9,10]. In this paper, we report the results of our further investigation on epoxidation of

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Abbreviations: H_2TDCPP, 5,10,15,20-tetrakis(*ortho*-dichlorophenyl)porphyrin; H_2TPFPP, 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin; $H_2TDCP(NO_2)_5P$, 2,3,7,12,17-pentanitro(*ortho*-dichlorophenyl) porphyrin; $H_2TPFP(NO_2)_4P$, 2,7,12,17-tetranitro(pentafluorophenyl)porphyrin

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PII: S1381-1169(99)00269-1

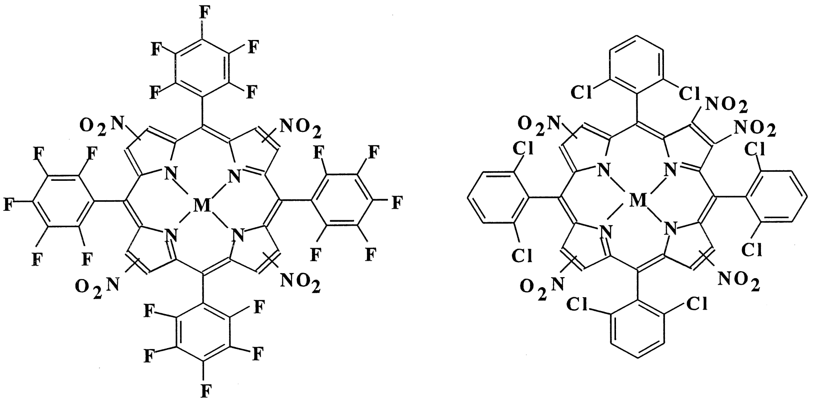

Fig. 1. Structure of the investigated metalloporphyrins.

cyclic alkenes with MMPP, a peracid previously used in *P*-450 model systems [11–18], and recently described [19] pernitrated metalloporphyrins as catalysts.

2. Experimental

The catalytic system consisting of the solution of metalloporphyrin (2.5×10^{-6} M), an alkene (3.45×10^{-4} M) and with/or without 4-*tert*-butyl-pyridine in ethyl acetate (1 ml) was mixed with an aqueous solution (2 ml) containing MMPP (7.0×10^{-4} M) and tetrabutylammonium chloride (1.0×10^{-5} M), used as phase transfer agent, under the atmosphere of argon at room temperature with mechanical stirring.

The second-generation porphyrin ligands, 5, 10,15,20-tetrakis(orthodichlorophenyl)porphyrin (H_2TDCPP) and 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (H_2TPFPP), were prepared by the classical Lindsey method by acid-catalyzed condensation of pyrrole and a suitable aldehyde [20]. These two porphyrin ligands were used as a starting material to prepare two other porphyrins with electron-withdrawing substituents at the β-pyrrole positions by reaction with fuming HNO_3 as described in Ref. [19]. The nitration of H_2TDCPP mainly gave pentanitro derivative $H_2TDCP(NO_2)_5P$ but the pentafluorinated ligand, H_2TPFPP, gave in this reaction a ligand with four nitro substituents, $H_2TPFP(NO_2)_4P$. The manganese, iron and cobalt derivatives of these ligands were obtained by conventional methods. This kind of metalloporphyrins, a third generation of robust metalloporphyrin catalysts with substituents on phenyls and electron-withdrawing NO_2 groups at the pyrrole positions, is shown in Fig. 1. Their purity was checked by taking UV–Vis and NMR spectra. MMPP, produced by Aldrich, contained 80% of the pure complex and the content of the active oxygen was checked by iodometric titration. Cyclooctene, cyclooctene oxide, cyclohexene, cyclohexene oxide, 2-cyclohexen-1-one, 4-*tert*-butyl-pyridine and *tert*-butylammonium chloride were obtained from Fluka. 2-Cyclohexen-1-ol and ethyl acetate were purchased from Aldrich.

Gas chromatographic analyses were performed with Chrom 5 gas chromatograph equipped with FID and columns filled with Carbowax 20M. UV–Vis spectra were recorded on Shimadzu UV-160A spectrophotometer.

3. Results and discussion

At first, we examined the epoxidation of *cis*-cyclooctene with six pernitrated metalloporphyrins as catalysts. As a result, we observed the formation of cyclooctene oxide only. Some of our results are shown in Table 1. As seen from this table, for manganese and iron catalysts, the conversion of the substrate and the selectivity are high even in the absence of 4-*tert*-butyl-pyridine. The systems with metalloporphyrins of the second generation, like Mn(TDCPP)Cl or Fe(TDCPP)Cl, are also active without a cocatalyst, but the addition of pyridine is necessary to obtain 100% conversion of cyclooctene [16]. The cobalt-pernitrated complex showed no activity as an epoxidation catalyst in the presence of MMPP, the cyclooctene conversion being at the level of the blank experiment. The catalytic performance of the investigated series of complexes was compared in the same reaction but in the presence of 4-*tert*-butyl-pyridine. This N-base has been reported to be one of the best possible axial ligands considering all the various parameters: nitrogen basicity, lipophilicity and oxidation resistance [21]. It is a well-known fact that the efficiency of the catalytic system depends on the presence of a cocatalyst, which decreases the electron density on the terminal oxygen and stabilizes metal-oxo species formed after transferring the oxygen atom to olefin. This has been shown to enhance the activity of the systems studied earlier [22]. As shown in Table 1, the addition of the cocatalyst slightly decreases the activity and selectivity of iron porphyrin and does not affect much the catalytic efficiency of manganese porphyrins. Thus, our present results indicate that iron and manganese porphyrins show high activity and selectivity even in the absence of any cocatalyst. It is interesting that cobalt porphyrin is completely unreactive without cocatalyst, but shows catalytic activity in the presence of 4-*tert*-butyl-pyridine. At present, it is not clear how the cobalt porphyrin with an N-base can lead to epoxidation when this metalloporphyrin alone does not catalyze this reaction.

Catalytic oxidation of cyclohexene with pernitrated complexes gave cyclohexene oxide as the only product (Table 2). No other products, e.g., those of allylic oxidation in the organic phase, were present, suggesting that no competing process of this type occurred, but products from opening the epoxide ring have been probably formed, accounting for the decreased selectivity. The conversion of the substrate was high, in particular for manganese and iron catalysts. The cobalt porphyrin was not active in this

Table 1
Epoxidation of cyclooctene by MMPP catalyzed by metallopophyrins[a]

[a] [Cyclooctene] = 3.45×10^{-4} M; [catalyst] = 2.5×10^{-6} M; [4-*t*-BuPy]:[catalyst] = 25:1; [MMPP] = 7.0×10^{-4} M; [Bu_4NCl] = 1.0×10^{-5} M; $t = 6$ min.

Metalloporphyrin [%]	4-*t*-BuPy	Olefin conversion [%]	Yield of epoxide [%]	Epoxide/catalyst [m/m]	Selectivity [%]
–	−	23.5	19.9	–	84.7
Mn(II)TDCPβ-$(NO_2)_5$P	−	100.0	93.9	129.6	93.9
Mn(II)TDCPβ-$(NO_2)_5$P	+	100.0	92.5	127.6	92.5
Fe(Cl)TDCPβ-$(NO_2)_5$P	−	100.0	92.2	127.2	92.2
Fe(Cl)TDCPβ-$(NO_2)_5$P	+	79.7	72.8	100.4	91.3
CoTDCPβ-$(NO_2)_5$P	−	1.7	–	–	–
CoTDCPβ-$(NO_2)_5$P	+	40.0	35.1	48.4	87.8
Mn(Cl)TPFPβ-$(NO_2)_4$P	−	100.0	95.4	131.6	95.4
Mn(Cl)TPFPβ-$(NO_2)_4$P	+	100.0	89.6	123.6	89.6
Fe(Cl)TPFPβ-$(NO_2)_4$P	−	100.0	91.6	126.4	91.6
Fe(Cl)TPFPβ-$(NO_2)_4$P	+	100.0	83.8	115.6	83.8
CoTPFPβ-$(NO_2)_4$P	−	8.0	5.5	7.5	68.1
CoTPFPβ-$(NO_2)_4$P	+	36.6	24.1	3.2	66.0

Table 2
Epoxidation of cyclohexene by magnesium monoperoxyphthalate catalyzed by metalloporphyrins[a]
[a][Cyclohexene] = 3.45×10^{-4} M; [catalyst] = 2.5×10^{-6} M; [4-*t*-BuPy]:[catalyst] = 25:1; [MMPP] = 7.0×10^{-4} M; [Bu_4NCl] = 1.0×10^{-5} M; *t* = 6 min.

Metalloporphyrin [%]	4-*t*-BuPy	Olefin conversion [%]	Yield of epoxide [%]	Epoxide/catalyst [m/m]	Selectivity [%]
–	−	24.6	18.8	–	76.7
Mn(Cl)TDCPβ-$(NO_2)_5$P	−	100.0	57.1	78.8	57.1
Mn(Cl)TDCPβ-$(NO_2)_5$P	+	100.0	63.8	88.0	63.8
Fe(Cl)TDCPβ-$(NO_2)_5$P	−	100.0	88.4	122.2	88.4
Fe(Cl)TDCPβ-$(NO_2)_5$P	+	61.5	58.3	80.7	94.8
CoTDCPβ-$(NO_2)_5$P	−	19.0	11.3	15.6	59.5
CoTDCPβ-$(NO_2)_5$P	+	70.0	69.6	96.0	99.2
Mn(Cl)TPFPβ-$(NO_2)_4$P	−	100.0	52.8	72.8	52.8
Mn(Cl)TPFPβ-$(NO_2)_4$P	+	100.0	73.3	101.2	73.3
Fe(Cl)TPFPβ-$(NO_2)_4$P	−	100.0	90.7	166.4	90.7
Fe(Cl)TPFPβ-$(NO_2)_4$P	+	97.0	72.2	99.6	74.6
CoTPFPβ-$(NO_2)_4$P	−	23.0	6.7	9.2	29.0
CoTPFPβ-$(NO_2)_4$P	+	44.5	29.9	41.2	66.9

system, but in the presence of 4-*tert*-butylpyridine, the conversion increased significantly, similarly as in the case of the cyclooctene. All these catalysts perform the epoxidation of cyclic olefins without significant destruction of the complexes. This confirms an efficient protection of the nitrated porphyrin derivatives against oxidative degradation.

It may be thus concluded that the character of the metal centre exerts a significant effect on the reactivity of the metalloporphyrins. Yields of the products varied with the metalloporphyrin applied. Manganese and iron porphyrins appeared to be much more active catalysts than the corresponding cobalt porphyrins. Only in the case of the cobalt porphyrin is the activity of the system enhanced by the presence of 4-*tert*-butyl-pyridine added in 25-fold excess over the catalyst concentration.

4. Conclusions

Our results indicate that pernitrated manganese and iron porphyrin catalysts are active and selective catalysts for the epoxidation of cyclic alkenes by MMPP. These results are significant because there are few examples in the literature of the pernitrated metalloporphyrins as oxidation catalysts. It is noteworthy that these systems catalyze the epoxidation of olefins also in the absence of a cocatalyst, i.e., species that can act as an axial ligand for the porphyrin, e.g., 4-*tert*-butylpyridine. Our system seems to be quite efficient in metal-catalyzed olefin epoxidation and offers various practical advantages such as mild conditions and the use of a highly stable and safe oxidant.

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