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Rapid and Highly Selective Epoxidation of Styrene by *meta*-Chloroperbenzoic Acid Catalyzed by Manganese *Meso*-tetrakis(Pentafluorophenyl)Porphyrin in the Presence of Tetrabutylammonium Acetate and Bromide

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Abstract Epoxidation of styrene with *m*-CPBA in the presence of Mn(TPFPP)Cl was improved to high yield (98–100%) and excellent selectivity (100%) by using *n*-Bu_4NOAc or *n*-Bu_4NBr as co-catalysts in less than 5 min. Also comparison of co-catalytic activity of *n*-Bu_4NOAc, *n*-Bu_4NBr and imidazole in epoxidation of *cis*-stilbene and styrene was carried out at similar conditions.

Keywords Epoxidation · Styrene · Catalysis · Metalloporphyrin · Co-catalytic effect

1 Introduction

Metalloporphyrin catalysts have been shown to be useful in olefin epoxidation by various oxidants such as PhIO [1, 2], NaOCl [3, 4], periodates [5–7], H_2O_2 [8–10], hydroperoxides [11], percarboxylic acids [12, 13], and *n*-Bu_4NHSO_5 (TBAO) [14]. *meta*-Chloroperbenzoic acid is used widely as an oxidant in organic synthesis and is often preferred to other proxy acids because of its relative ease of handling. Among olefins epoxidation of styrene to styrene oxide is of particular interest from both scientific and commercial point of view [15, 16]. However the formation of desired product (styrene oxide) is always accompanied by the oxidative cleavage of double bond to benzaldehyde and isomerisation of styrene oxide to phenyl acetaldehyde [17, 18]. Achieving high selectivities, excellent yields and mechanism elucidations are of interest for these catalytic epoxidations. Also it was found that the employment of co-catalysts such as pyridines, imidazoles and quaternary ammonium salts results in a significant change of catalytic activity of metalloporphyrins, in particular Manganese(III) porphyrins catalysts [19–30].

The epoxidation of olefins with Manganese(III)(TPFPP) (TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrin) and *n*-Bu_4NHSO_5 were carried out in the presence of tetrabutylammonium salts. The best yields and selectivities have been achieved by the addition of *n*-Bu_4NOAc as co-catalyst. Yields and epoxide selectivities were low when *n*-Bu_4NBr was used as co-catalyst [31].

Here we described the complete conversion and highly selective epoxidation of styrene with *meta*-chloroperbenzoic (*m*-CPBA) catalyzed by Mn(TPFPP)Cl (TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrin) in the presence of *n*-Bu_4NOAc or *n*-Bu_4NBr as co-catalyst in CH_2Cl_2 in less than 5 min at room temperature. Also co-catalytic activities of *n*-Bu_4NOAc and *n*-Bu_4NBr were compared to imidazole (ImH) (as a nitrogen donor ligand) in the epoxidation of *cis*-stilbene and styrene using *m*-CPBA and Mn(TPFPP)Cl.

2 Experimental

2.1 Material

The free base porphyrins $TPPH_2$ [32], $TPFPPH_2$ [33], were prepared and purified as reported previously. Mn(TPP)Cl was synthesized using $MnCl_2{\cdot}4H_2O$ according to the procedure of Adler et al. [34]. The synthesis of Mn(TPFPP)Cl was based on the procedure given by Kadish et al. [35]. Imidazole was purchased from Merck. *n*-Bu_4NOAc was prepared by adding tetrabutylammonium hydrogen sulfate (6.5 mmol) to a solution of sodium acetate (32.5 mmol) in

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water (40 mL), the mixture was stirred for 30 min and then extracted with CH_2Cl_2 (80 mL) and the extract was dried over magnesium sulfate. After filtration and evaporation of the solvent, the remaining paste was washed with hexane (10 mL) and dried under vacuum. Styrene was purified by passing through a column of silica gel. *m*-CPBA (as 70% solution in water) and other substrates were purchased from Aldrich or Fluka and were used as received.

2.2 General Oxidation Procedure

Stock solutions of MnPor catalysts (0.003 M) were prepared in CH_2Cl_2. In a typical reaction 0.001 mmol (0.3 mL) of catalyst, 0.1 mmol of alkene and x mmol (as required) of co-catalyst were dissolved in 0.2 mL of CH_2Cl_2. *m*-CPBA (0.2 mmol) was then added to the reaction solutions at 25 °C. The reaction solutions were stirred for the required times. In the case of styrene, the reaction solutions were analyzed immediately by GLC. For *cis*-stilbene, the solvent of the reaction solution was removed under reduced pressure, *n*-hexane (2 mL) was added, the resulting mixture was filtered and *n*-hexane was removed under vacuum. The identification and the quantification of the products were done by ^1H NMR spectroscopy (in $CDCl_3$).

3 Results and Discussion

3.1 Comparison of Co-catalytic Effects of ImH and Tetrabutylammonium Salts on the Styrene Epoxidation Using Mn(TPFPP)Cl and Mn(TPP)Cl

In Table 1 we compiled the data for the epoxidation of styrene with *m*-CPBA. *m*-CPBA alone yields a mixture of 9% benzaldehyde, 24% phenylacetaldehyde and 18% styrene oxide (conversion = 51%; epoxide selectivity = 35%). Addition of Mn(TPFPP)Cl alone had no noticeable effect on the conversion and selectivity of styrene epoxidation reaction (conversion = 55%; epoxide selectivity = 34%). Using *m*-CPBA/Mn(TPFPP)Cl in association of a tetrabutylammonium salt with a noncoordinating anion (*n*-Bu_4NBF_4) as co-catalyst had a little effect on the conversion and selectivity of this reaction (conversion = 59%; epoxide selectivity = 43%). But using tetrabutylammonium salts with the coordinating anions (*n*-Bu_4NBr and *n*-Bu_4NOAc) as co-catalyst remarkably improved the conversion and selectivity of this reaction (for *n*-Bu_4NOAc conversion = 100% in 1 min and for *n*-Bu_4NBr conversion is 98% in 5 min; epoxide selectivity for both of them is 100%). The relative co-catalytic activities of OAc^- and Br^- could be rationalized based on their intrinsic basicities and steric properties. pK_a for HOAc and HBr are 4.76 and −9.00 respectively. Steric bulk for Br is more than O regarding their atomic radii. So OAc^- should be a better co-catalyst compared to Br^-. The total turnover numbers for epoxidation of styrene with *m*-CPBA/Mn(TPFPP)Cl in association of *n*-Bu_4NOAc and *n*-Bu_4NBr were 907 and 903, respectively.

When the same reaction was performed in the presence of ImH as co-catalyst under the co-catalyst/Mn(TPFPP)Cl molar ratio mentioned in Table 1, the selectivity was 100% but the conversion was to some extent lower relative to non-catalyzed reaction (conversion reaches 42% in 1 min and was nearly unchanged after 2 h).

Table 2 shows the effect of different co-catalyst/Mn(TPFPP)Cl molar ratios on the conversion and selectivity of styrene epoxidation reaction. When *n*-Bu_4NOAc was used as co-catalyst, the conversion was excellent (100%) at all co-catalyst/Mn(TPFPP)Cl molar ratios (10–150), but the epoxide selectivity was improved with increasing the co-catalyst/catalyst ratio (100% at the molar

Table 1 Epoxidation of styrene with *m*-CPBA catalyzed by Mn(TPFPP)Cl in the presence of different co-catalyst

Entry	Co-catalyst	Conversion (%)	Styrene oxide (%)	Benzaldehyde (%)	Phenylacetaldehyde (%)	Epoxide selectivity (%)
1[a]	–	51	18	9	24	35
2	–	55	19	13	23	34
3	*n*-Bu_4BF_4	59	25	4	30	43
4[b]	ImH	(42) 44	(42) 44	–	–	(100) 100
5	*n*-Bu_4Br	(85) 98	(85) 98	–	–	(100) 100
6	*n*-Bu_4OAc	(100)	(100)	–	–	(100)

Reactions were run at least in triplicate under air at 25 ± 2 °C, and the data represent an average of these reaction with ±10%. The molar ratio for catalyst–co-catalyst–styrene–oxidant were 1:100:100:200 and [Mn(TPFPP)Cl] = 9×10^{-4}. Conversions and yields are determined after a reaction time of 5 min and results corresponding to 1 min are put in parentheses. The GC conversions (%) to the products and the epoxide yields (%) were measured relative to the starting alkene

[a] The data are obtained by *m*-CPBA alone

[b] Styrene conversion ends after 5 min

Table 2 Styrene epoxidation % for ImH and n-Bu_4NOAc as co-catalyst in association with Mn(TPFPP)Cl catalyst under different co-catalyst/catalyst ratios

Ratios	Conversion (%)	Epoxide (%)	Phenylacetaldehyde (%)	Epoxide selectivity (%)
10	100 (93)	44 (32)	56 (61)	44 (34)
20	100 (86)	57 (33)	43 (53)	57 (37)
70	100 (76)	98 (37)	2 (39)	98 (49)
100	100 (42)	100 (42)	–	100 (100)
150	100 (27)	100 (27)	–	100 (100)

All the reaction conditions were the same as those described in Table 1 in 1 min. The GC conversions (%) or epoxide yields (%) were measured relative to the starting alkene. The data outside of the *parentheses* refer to n-Bu_4NOAc co-catalyst and those inside the parentheses relate to ImH

ratio 100). When ImH was used as co-catalyst, although increasing the co-catalyst/catalyst ratio improved the selectivity (34% at co-catalyst/catalyst ratio 10; 100% at co-catalyst/catalyst ratio 100), but it had a deleterious effect on styrene conversion (93% at co-catalyst/catalyst ratio 10; 27% at co-catalyst/catalyst ratio 150).

Therefore we concluded that ImH should have been oxidized in a competitive reaction at higher concentrations, although, the possibility of the formation of catalytically inactive six-coordinate manganese complex, $[Mn(TPFPP)(ImH)_2]^+$, cannot be ruled out [36–40]. n-Bu_4NOAc clearly showed better co-catalytic activity than ImH at all co-catalyst/Mn(TPFPP)Cl molar ratios considering both conversion % and selectivity %.

Epoxidation of styrene by *m*-CPBA in association of Mn(TPP)Cl (TPP = *meso*-tetraphenylporphyrin) with a non electron deficient porphyrin ligand was carried out in the presence of n-Bu_4NOAc, n-Bu_4NBr and ImH (Table 3). Although the existence of these co-catalysts improves the selectivity of epoxidation reaction, especially in the case of n-Bu_4NOAc, they have no considerable effects on the conversion. Mn(TPP)Cl was less effective catalyst compared to Mn(TPFPP)Cl under these experimental conditions. Furthermore, in the case of Mn(TPP)Cl the degradation of the catalyst occurred before the completion of olefin conversion and the existence of these co-catalysts has no noticeable effect on the stability of this catalyst [41–43].

Table 3 Epoxidation of styrene with *m*-CPBA catalyzed by Mn(TPP)Cl in the presence of n-Bu_4NOAc, n-Bu_4NBr and ImH in CH_2Cl_2

Co-catalyst	Conversion (%)	Styrene oxide (%)	Epoxide selectivity (%)
ImH	50	26	51
n-Bu_4NOAc	54	49	90
n-Bu_4NBr	49	26	53
–	53	17	31

All the reaction conditions were the same as those described in Table 1 in 5 min. The GC conversions (%) or epoxide yields (%) were measured relative to the starting alkene. Conversions and yields are determined after a reaction time of 5 min

3.2 Comparison of Co-catalytic Effects of ImH, n-Bu_4NOAc and n-Bu_4NBr on the *cis*-stilbene Epoxidation in the Presence of Mn(TPFPP)Cl

Epoxidation of *cis*-stilbene with *m*-CPBA catalyzed by Mn(TPFPP)Cl was performed as a probe [44–46] for better comparison of co-catalytic activities of imidazole, n-Bu_4NBr and n-Bu_4NOAc (Table 4). In the presence of imidazole, *cis*-stilbene oxide (conversion = 41%) was obtained predominantly with only a trace amount of *trans*-stilbene oxide. The epoxidation was preceded with lower stereoselectivity in the presence of both n-Bu_4NOAc and n-Bu_4NBr. *Cis*-stilbene was disappeared completely with *m*-CPBA under the reaction conditions and led to similar *cis*/*trans*-stilbene oxide in the presence of n-Bu_4NOAc (92/8) and n-Bu_4NBr (96/4). It seems that the active oxidizing species are the same for n-Bu_4NOAc and n-Bu_4NBr and are different for imidazole.

3.3 Active Oxidant

In the preliminary studies on the oxidation of manganese porphyrins by acylhydroperoxide, Groves described the observation of a (acylperoxo)manganese(III) complex and the corresponding several different high valent oxomanganese species at a very low temperature [12]. In our study for the oxidation of Mn(TPFPP)Cl by *m*-CPBA, UV–Vis spectroscopy revealed a different spectrum evolution in the presence of ImH, n-Bu_4NOAc or n-Bu_4NBr at room temperature. Addition of ImH (6×10^{-4} mmol) and then *m*-CPBA (1.2×10^{-3} mmol) to a solution of Mn(TPFPP)Cl (6×10^{-6} mmol in 0.5 mL CH_2Cl_2) showed no change in

Table 4 Epoxidation of *cis*-stilbene with *m*-CPBA catalyzed by Mn(TPFPP)Cl in the presence of n-Bu_4NOAc, n-Bu_4NBr and ImH in CH_2Cl_2

Co-catalyst	Conversion (%)	*Cis*-stilbene oxide (%)	*Trans*-stilbene oxide (%)
ImH	41	41	Trace
n-Bu_4NOAc	100	92	8
n-Bu_4NBr	100	96	4

All the reaction conditions were the same as those described in Table 1 in 1 min for n-BuN_4OAc and 5 min for ImH and n-BuN_4Br. The solvent was removed in vacuo, the products and unreacted alkene were extracted with n-hexane. The isomer ratios were determined by ^1H NMR spectroscopy

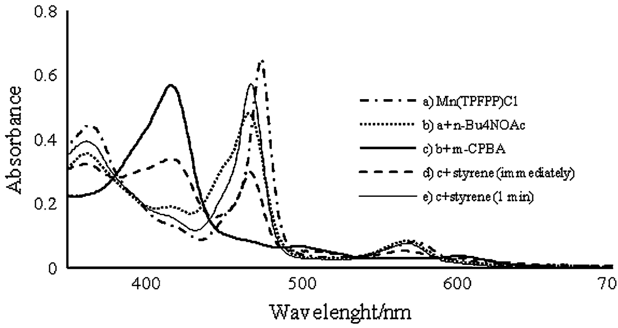

Fig. 1 UV–Vis absorption spectra recorded at room tempreature: (*a*) for Mn(TPFPP)Cl (6 × 10^{-6} mmol) in CH_2Cl_2 (0.5 mL); (*b*) after the addition of *n*-Bu_4NOAc (6 × 10^{-4} mmol); (*c*) after the addition of *m*-CPBA (1.2 × 10^{-3} mmol) to this mixture (*d*); immediately after the addition of styrene (6 × 10^{-3} mmol) to the last mixture (*e*) after 1 min

the Soret band at 474 nm and no sign of formation of Mn-oxo species. But by adding *n*-Bu_4NOAc (6 × 10^{-4} mmol) to a CH_2Cl_2 solution of Mn(TPFPP)Cl, the Soret band was considerably hypsochrome shifted ($\lambda_{max} = 469$ nm) due to the formation of a six coordinate $[Mn(TPFPP)(OAc)_2]^-$ species [31] (Fig. 1a, b). Addition of *m*-CPBA (1.2 × 10^{-3} mmol) to this solution caused the appearance of a long lived (>2 h) intense Soret band at $\lambda_{max} = 412$ nm, which is presumably due to Mn-oxo species (Fig. 1c) [12, 13, 29, 47]. This intense band was decayed rapidly by the addition of styrene (Fig. 1d, e).

Also the reaction of Mn(TPFPP)Cl (6 × 10^{-6} mmol in 0.5 mL CH_2Cl_2) and *m*-CPBA (1.2 × 10^{-3} mmol) was carried out in the presence of a mixture of ImH (6 × 10^{-4} mmol) and *n*-Bu_4NOAc (6 × 10^{-4} mmol). UV-Vis spectroscopy showed that the Mn-oxo species were formed at first but disappeared after 15 min, indicating that the formed Mn-oxo species were consumed by ImH.

Similarly addition of *m*-CPBA to a solution of Mn(TPFPP)Cl and *n*-Bu_4NBr generated a new bond at $\lambda_{max} = 409$ nm which its lifetime was much shorter (20 min) than that of in the presence of *n*-Bu_4NOAc. Thus it seems plausible that for *n*-Bu_4NOAc and *n*-Bu_4NBr co-catalysts, the highly stable Mn-oxo species is the primary active oxidant, whereas in the case of ImH the functional oxidant is predominantly the six coordinate $[Mn(TPFPP)(ImH)(m\text{-}CPBA)]^+$ with some possible contributions made by very unstable transient species.

4 Conclusion

In summary, Mn(TPFPP)(Cl) in association of *n*-Bu_4NOAc or *n*-Bu_4NBr could effectively catalyze the epoxidation of olefins with *m*-CPBA regarding both conversion and selectivity, although *n*-Bu_4NOAc is a better co-catalyst. Also ImH could help improving the selectivity of alkene epoxidation by this catalytic system, but has a negative effect on the conversion. This catalytic system shows excellent stability toward its oxidation.

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