Catalytic Alkene Epoxidation with Hydrogen Peroxide in the Presence of 5,10,15,20-Tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrinatomanganese(III) Acetate and Imidazole†

Daryoush Mohajer* and Hassan Hosseini Monfared

Department of Chemistry, Shiraz University, Shiraz, 71454, Iran

Different alkene epoxidations were performed with aqueous hydrogen peroxide (35%) in MeCN with low to very high conversions and good to excellent selectivities by 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrinato-manganese(III) acetate and imidazole at room temperature.

The development of new catalytic systems for epoxidation of alkenes under mild conditions is an important subject in chemistry and very efficient model systems for alkene epoxidation, based on cytochrome P-450-dependent mono-oxygenases, using various manganese porphyrin catalysts and different oxidants have been reported.[1] The water soluble Mn(TDCSPP)Cl and Fe(TDCSPP)Cl [TDCSPP = tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin] complexes have been used for a variety of oxidations and bond cleavages,[2] and also for kinetic, electrochemical and dynamic studies.[3] However, there are only a few reports of alkene epoxidation either by unsupported or supported forms of these catalysts in association with ClO⁻ and PhIO oxidants.[4,5] To our knowledge attempts to use hydrogen peroxide for epoxidation of alkenes by supported [Mn(TDCSPP)(OAc)] on cationic ion-exchange resins[5] and on montmorillonite K10[6] have been unsuccessful. Herein we describe for the first time the efficient homogeneous epoxidation of alkenes by the [Mn(TDCSPP)(OAc)]–imidazole–H_2O_2 system in MeCN by maintaining an excess amount of the oxidant throughout the reaction.

Results of oxygenation of various alkenes are given in Table 1. Different conversions (21–100%) and greater than 90% selectivities (except for cyclopentene) are observed for epoxidation of alkenes within 20 to 120 min. In the epoxidation of cycloalkenes, selectivity is decreased on decreasing the ring size. While cyclooctene was almost quantitatively oxidised to cyclooctene oxide, selectivities for epoxidation of cyclohexene and cyclopentene were 90 and 82%, respectively, with the allylic ketones and alcohols as the side products. Apparently smaller rings are more prone to oxidation at allylic positions.[7] Oxidation of styrene led to 76% of styrene oxide with 97% selectivity and 2% of benzaldehyde in 120 min. Epoxidation of *cis*-stilbene pro-

Table 1 Epoxidation of alkenes with H_2O_2 catalysed by Mn(TDCSPP)(OAc)–imidazole[a]

Substrate	Conversion (%)[b]	Epoxide yield (%)[b]	Selectivity (%)[c]	Time (min)
Cyclooctene	51	50	98	20
Cyclohexene	94	85	90	90
Cyclopentene	100	82	82	40
Styrene	78	76	97	120
cis-Stilbene	42	21 (*cis*)	50	120
		21 (*trans*)	50	
trans-Stilbene	15	15 (*trans*)	100	120
Hept-1-ene	21	21	100	120
Indene	92	92	100	120

[a]Reaction conditions: to a solution containing alkene (1.77 mmol), Mn(TDCSPP)(OAc) (0.00113 mmol) and imidazole (0.82 mmol) in 3 ml of MeCN, 35% aqueous hydrogen peroxide (2 ml, 22 mmol) was added dropwise over a period of 5 min, under air at 28 ± 2 °C. [b]GLC conversions and yields are based on the starting substrates. [c]Selectivity = [epoxide yield (%)/conversion (%)] × 100.

ceeded with 42% conversion within the same period and resulted in a 1:1 mixture of *cis*- and *trans*-stilbene oxides, whereas oxidation of *trans*-stilbene produced only *trans*-stilbene oxide. The terminal alkene hept-1-ene showed poor reactivity (21% conversion) and very high selectivity (100%) for epoxidation.

Table 2 gives the results of epoxidation of cyclohexene by H_2O_2 under various conditions. When oxidation reaction was performed in MeCN with a cyclohexene: Mn(TDCSPP)(OAc):imidazole:H_2O_2 ratio of 1566:1:728:20000, 90% conversion with 91% selectivity for epoxidation was observed in 1 h, whereas oxygenation in dimethyl-formamide (DMF) as a solvent led almost to the same conversion (92%) but epoxide selectivity was lower (79%). When MeCN was replaced by MeOH a much lower con-

Table 2 Epoxidation of cyclohexene under different conditions

Conditions	Conversion (%)[b]	Epoxide yield (%)[b]	Selectivity (%)[c]	Time (h)
Complete system[a]	90	82	91	1
Without Mn(TDCSPP)(OAc)	1	<1		5
Without imidazole	5	3	60	2
MeCN replaced by DMF	92	73	79	1
MeCN replaced by MeOH	52	45	87	1
MeCN replaced by H_2O[d]	27	27	100	1

[a]To a solution containing cyclohexene (1.77 mmol), Mn(TDCSPP)(OAc) (0.00113 mmol) and imidazole (0.82 mmol) in 3 ml of MeCN, 35% aqueous hydrogen peroxide (2 ml, 22 mmol) was added dropwise over a period of 5 min, under air at 28 ± 2 °C, [b,c]See Table 1. [d]0.59 mmol of cyclohexene was used.

version (52%) was obtained. The use of the highly polar H_2O with very poor solubility for cyclohexene as a reaction medium gave the lowest conversion. When the oxidation reaction was performed in MeCN but in the absence of

imidazole, a dramatic decrease in epoxide yield (3%) and selectivity (60%) was observed. Both direct coordination of imidazole to the active manganese center (proximal effect) and its action as a base (distal effect) may facilitate the heterolytic cleavage of the O–O bond in Mn^{III}–O–OH species.[8] The possibility of involvement of peroxyimidic acid, as an oxygen donor, was excluded in the oxidation reactions performed in MeCN, as no $MeCONH_2$ was observed by the direct treatment of H_2O_2 and MeCN, under the catalytic oxidations in the absence of any substrate.[9] Exclusion of Mn(TDCSPP)(OAc) catalyst from the oxidation system gave practically no epoxide after 5 h.

It should be noted that Mn(TDCSPP)(OAc) alone and particularly in combination with imidazole effectively catalyses the decomposition of hydrogen peroxide.[3a,8] Thus, it was necessary to add a large excess of H_2O_2, from the start, in order to achieve good yields in the oxygenation reaction, in a reasonable time.

In conclusion the water soluble and highly stable Mn(TDCSPP)(OAc) complex can efficiently catalyse the epoxidation of alkenes with environmentally clean hydrogen peroxide in the presence of imidazole cocatalyst in MeCN. Solvents of moderate polarity show good potential as a medium for this catalytic system.

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