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Highly selective olefin epoxidation with the bicarbonate activation of hydrogen peroxide in the presence of manganese(III) *meso*-tetraphenylporphyrin complex: Optimization of effective parameters using the Taguchi method

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ABSTRACT

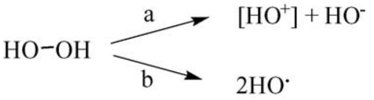
A Mn^{III}-porphyrin-based catalytic system was explored for olefin epoxidations under mild reaction conditions using sodium bicarbonate–hydrogen peroxide as an oxidant. The Mn(TPP)OAc/imidazol/$NaHCO_3$ system efficiently catalyzed the epoxidation of olefins with H_2O_2. Cyclic olefins were transformed in excellent yield (80–100%) and selectivity (87–100%), the obtained selectivity and yields being much better than those observed in the absence of bicarbonate. In the presence of an excess of substrate, the turnover number 4286 was obtained with the Mn(TPP)OAc/Im/$NaHCO_3$/H_2O_2 system after 2 h. The bicarbonate-activated oxidation system is a simple, inexpensive, and relatively nontoxic alternative to other oxidants and peroxyacids, and it can be used in a variety of oxidations where a mild, neutral pH oxidant is required.

Due to the various factors, such as solvent, reaction temperature, stoichiometric ratio of imidazole/$NaHCO_3$/H_2O_2, influencing the oxidation of olefins, the Taguchi method of system optimization was used to determine the percent of contribution (%*P*) of each factor. It was found that the solvent had the most influence on the oxidation (30.051%) and the imidazole amount stood in second place (22.286%).

1. Introduction

The catalytic epoxidation of olefins has been a subject of growing interest in the production of chemicals and fine chemicals since epoxides are the key starting materials for a wide variety of products [1,2]. Much effort has been made to develop new active and selective epoxidation catalysts for those processes that require an elimination of by-products. A wide variety of metal complexes have been synthesized for this purpose and their catalytic properties have been extensively studied [3–10]. This transformation using environmentally benign oxidants has aroused much interest, because the chemical industry continues to require cleaner oxidation, which is an advance over environmentally unfavored oxidations and a step up from more costly organic peroxides.

Manganese *meso*-tetrakisaryl porphyrins and several other metal porphyrin complexes have been studied intensively as catalysts in epoxidation reactions of alkenes [11,12]. A variety of oxidants such as iodosylarenes, alkylhydroperoxides, peracids and hypochlorite in addition to H_2O_2 were employed [11,12]. Of the above oxygen donors, hydrogen peroxide provides a reasonably cheap, readily available oxidant, giving only water as a by-product. However, it is necessary for efficient epoxidation that the hydrogen peroxide should be cleaved heterolytically to give an 'oxene' (reaction (1a))



(1)

rather than homolytically to give hydroxyl radicals (reaction (1b)). The formation of hydroxyl radicals leads to somewhat indiscriminate oxidation of organic substrates, with hydrogen abstraction being important. In a reaction of type (1a), in which an oxene or its equivalent is involved, oxidation is much more selective and, with olefins, leads directly to epoxides. There have been investigations concerning the hetero- and homolytic cleavage of hydroperoxides and hydrogen peroxide in the presence of various metalloporphyrins. The early porphyrin-based catalysts often showed rapid deactivation due to the oxidative degradation of the ligand [13–16]. Spectacular improvements in the robustness and activity of catalysts for olefin epoxidation and hydroxylation of alkenes were obtained after the introduction of halogen substituents into the porphyrin ligands [17]. General disadvantages of manganese

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porphyrin-based epoxidation catalysts are the difficulty in preparing the ligands and the often tedious purification that is required.

Hydrogen peroxide has a high active oxygen content compared to other stoichiometric oxidants, that is peroxycarboxylic acids, periodate, and peroxymonosulfate [18]. Hydrogen peroxide is a widely used oxidant with high active oxygen content [19–21], but it is a rather slow oxidizing agent in the absence of activators. Epoxidation of alkenes by HCO_3^-/H_2O_2 in CD_3CN/D_2O [22] has been described but the reaction time is high (24 h) and the conversion of α-methylstyrene is only 50%. In another study hydrogen peroxide was electrogenerated *in situ* in aqueous bicarbonate solutions and has been used for water soluble alkenes using Mn^{2+} as the catalyst [23]. $MnSO_4/NaHCO_3/H_2O_2/^tBuOH$ system has been used for epoxidation of alkenes [24] in 16 h as well. A number of groups have discussed the use of catalysts containing species such $Mo(CO)_6$ immobilized in a polymer bound aliphatic amine [25], complexes of oxodiperoxo-8-hydroxy-quinolinolato Mo(VI) over mesoporous silica [26], oxodiperoxo molybdenum(VI) complex $[MoO(O_2)_2(saloxH)]$ (saloxH$_2$ = salicylaldoxime) [27] and hexathiocyanatorhenate(IV) $(Ph_4P)_2[Re(NCS)_6]$ [28] in the presence of the $H_2O_2/NaHCO_3$ system as an oxidant in the oxidation of olefins. Simple metal salts like Mn^{2+}, Cr^{2+}, Fe^{3+} and Mn-porphyrins with $NaHCO_3/H_2O_2$ are used for olefin epoxidation. Halogenated porphyrins were required to resist oxidation of the catalysts [29]. Ammonium bicarbonate has been used for diastereoselective epoxidation of allylically substituted alkenes using sterically bulky metalloporphyrins as catalyst provides high trans-selectivities (i.e., *trans*:*cis*-epoxide ratio) [30].

The catalysis of sulfide oxidation by bicarbonate ions, bicarbonate ion catalysis of methionine oxidation to methionine sulfoxide by H_2O_2 in water [31], and bicarbonate-catalyzed hydrogen peroxide oxidation of cysteine and related thiols to the corresponding disulfides [32] have also been reported.

Such systems can have one or more disadvantages, such as the long reaction time [22,24], need to complex catalysts like the sterically bulky metalloporphyrins that are not easy to make [29,30] and low selectivity and by-products like diol [22]. Our interest in the development of methods to accomplish selective oxidation of olefins led us to consider another little-explored mode of reactivity for the formation of epoxides through the use of $NaHCO_3/H_2O_2$/Imidazole/Mn(TPP)OAc catalysis. In this paper, we describe our studies aimed at catalyzing efficient oxygen transfer from hydrogen peroxide to olefins using the $H_2O_2/NaHCO_3$ system as the source of oxygen and using the statistical Taguchi design to obtain the optimum oxidation condition.

2. Experimental

2.1. Materials and equipment

Manganese(II) acetate tetrahydrate was purchased from Sigma. Hydrogen peroxide (30% in water) was supplied by Merck and stored at 5 °C, and was periodically titrated to confirm its purity. The exact concentration of hydrogen peroxide was determined by titration with potassium permanganate. Solvents of the highest grade commercially available (Merck) were used without further purification. The olefins and other reagents were purchased from Merck and Fluka and used as received. The free base porphyrin H_2TPP was prepared and purified by the method reported previously [33]. Manganese insertion into this free base porphyrin was carried out using the method of Adler et al. [34]. Fig. 1 shows the structure of the Mn-porphyrin complex used in this study.

The reaction products of oxidation were determined and analyzed by an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 μm × 320 μm × 0.25 μm) with flame-ionization detector and gas chromatograph–mass spectrometry (Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector). ^{1}H NMR spectra were recorded by using Bruker 250 MHz spectrometer. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. The electronic transition spectra were recorded on a Thermospectronic model α, UV–vis spectrometer with 1 cm quartz cells was used for recording and storage of UV–vis absorbance spectra.

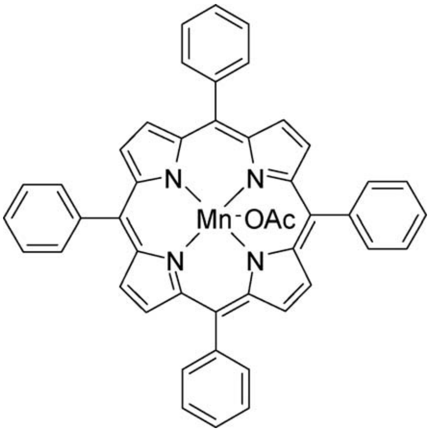


Fig. 1. Mn(TPP)OAc employed in this study.

2.2. Oxidation reactions

Reactions were carried out in a 25 ml round bottom flask. Based on our previous work from catalytic oxidation of olefins by the catalyst/imidazole/oxidant/solvent system [35] and some preliminary experiments, in a typical experiment, H_2O_2 (1–10 mmol) was added to a flask containing the Mn(TPP)OAc (1.4×10^{-3} mmol), cyclooctene (1 mmol) and $NaHCO_3$ (0.26–5.25 mmol) in solvent (3 ml). Reactions were carried out for 6 h, under magnetic stirring at room temperature. At appropriate intervals, aliquots were removed and quantified immediately by GC. Imidazole (7–21 μmol) was added to some reactions. The oxidation products were identified by comparing their retention times with those of authentic samples or alternatively by ^{1}H NMR and GC–Mass analyses. Yields are based on the added olefin and were determined by a calibration curve. Control reactions were carried out in the absence of catalyst, under the same conditions as the catalytic runs. No products were detected.

3. Results and discussion

3.1. Oxidation of cyclooctene

In the first instance, the effect of various reagents was evaluated in the catalytic oxidation of cyclooctene in the presence of Mn(TPP)OAc with hydrogen peroxide as an oxidant. All reactions were carried out with 1 mmol of cyclooctene in CH_3CN and in the presence of 1.4 μmol catalyst at room temperature for 5 h. Cyclooctene oxide was the sole product. The results are summarized in Table 1. The results of control experiments revealed that the oxidation of cyclooctene in the absence H_2O_2 does not occur. As reported by Mansuy [17] due to oxidative degradation of the Mn(TPP)OAc catalyst, the epoxide yield by Mn(TPP)OAc/Im was very low (Table 1, run no. 1). Interestingly, an improvement in the cyclooctene conversion was observed when imidazole was replaced with sodium bicarbonate (epoxide yield 5%, Table 1, run no. 2). The mixture of imidazole/$NaHCO_3$ catalyzed

Table 1
Control experiments in oxidation of cyclooctene by H_2O_2[a].

Run	Catalyst	Co-catalyst	Activator	Conversion (%)	Epoxide yield (%)
1	Mn(TPP)OAc	Imidazole	None	<1	<1
2	Mn(TPP)OAc	None	$NaHCO_3$	5.0	5.0
3	None	Imidazole	$NaHCO_3$	15	15
4	None	None	$NaHCO_3$	3	3
5	Mn(TPP)OAc	Imidazole	$NaHCO_3$	43	43

[a] *Reaction conditions*: catalyst (1.4 μmol), cyclooctene (1.0 mmol), CH_3CN (3 ml), Im (14 μmol), $NaHCO_3$ (0.07 mmol), H_2O_2 (5.0 mmol), reaction time (5 h) at room temperature. Conversions and yields are based on starting cyclooctene.

the cyclooctene oxidation up to yield 15% with H_2O_2 in the absence of Mn(TPP)OAc (Table 1, run no. 3). $NaHCO_3$ by itself produced only 3% of the epoxide (Table 1, run no. 4). Whether the improvement effect of $NaHCO_3$ was a catalyst-stabilizing effect or from the formation of peroxymonocarbonate ion was not clear. However, the most striking catalytic enhancement giving a significant quantity of cyclooctene oxide was with Mn(TPP)OAc/Im/$NaHCO_3$ (yield 43%, Table 1, run no. 5). Of these three systems, the Mn(TPP)OAc/Im and Mn(TPP)OAc/$NaHCO_3$ catalysts were discounted due to the low yield of the epoxide. Thus, the remaining Mn(TPP)OAc/Im/$NaHCO_3$ system was optimized.

The results of the control experiments led us to conclude that by optimization of H_2O_2, imidazole, solvent, $NaHCO_3$ and reaction time it is possible to obtain a high yield of epoxide in a short time and to get insight into the relative importance of each factor. In the search for suitable reaction conditions to achieve the maximum oxidation of cyclooctene, the Taguchi method was used.

3.2. Taguchi experiment design

In addition to the nature of catalyst and olefin concentration, concentrations of axial ligand (imidazole), activator (sodium hydrogencarbonate), solvent and oxidant (hydrogen peroxide) influence the catalytic oxidation of olefins. The essential feature of catalytic oxidation is to give a high epoxide yield and selectivity at short time. Therefore, in order to achieve a high epoxide yield and relatively fast oxidation, understanding the relationship between the different system parameters and the oxidation time of the olefins is essential. In the oxidation of olefins by catalytic methods, however, there are many parameters that are important to obtain high epoxide yields. The interrelationships between the parameters are complex, and the conventional approach of experimenting with one variable (or one factor) at a time is labor-intensive and time consuming. Hence, the analyses using conventional experimental methods are sometimes inefficient. Therefore, the Taguchi method [36] was introduced in this work. The Taguchi method determines the experimental condition having the least variability as the optimum condition. The variability can be expressed by a signal to noise (S/N) ratio [36]. The experimental condition having the maximum S/N ratio is considered as the optimal condition.

Table 2
Parameters and their values corresponding to their levels to be studied in the experiments.

Parameter	Levels			
	1	2	3	4
A. Imidazol (μmol)	0	7	14	21
B. $NaHCO_3$ (mmol)	0.26	0.35	0.53	5.25
C. Solvent	a	b	c	d
D. H_2O_2 (mmol)	1	3	5	10
E. Time (h)	1	2	3	4

a, MeOH; b, CH_2Cl_2; c, $CHCl_3$; d, CH_3CN.

Based on our previous work from catalytic oxidation of olefins by the catalyst/imidazole/oxidant/solvent system [35] and the results of Table 1, the main operational parameters and their levels were selected and showed in Table 2.

The design of experiments is an approach for systematically varying the controllable input factors and observing the effects of these factors on the output product parameters. The assumption used in this study was that the individual effects of the input factors on the output product parameters are separable. That means the effect of an independent variable on the performance parameter does not depend on the different level settings of any other independent variable. The orthogonal

Table 3
Experimental layout of cyclooctene oxidation using the L16 orthogonal array and experimental results for percent of epoxide yield.

Experimental number	A	B	C	D	E	Epoxide yield (%)			
						First 1	Second 2	Third 3	S/N
1	1	1	1	1	1	11.2	11	11.5	21.006
2	1	2	2	2	2	1	2	1.3	2.119
3	1	3	3	3	3	37.8	36	37	31.343
4	1	4	4	4	4	48.9	49.4	48	33.761
5	2	1	2	3	4	37	35.8	36.3	31.212
6	2	2	1	4	3	56	59	58	35.212
7	2	3	4	1	2	47.7	47	48.6	33.580
8	2	4	3	2	1	12.1	11.7	12	21.532
9	3	1	3	4	2	51	50.8	51	34.140
10	3	2	4	3	1	51.5	50	51	34.121
11	3	3	1	2	4	61.6	59	60.9	35.631
12	3	4	2	1	3	20	17	19	25.361
13	4	1	4	2	3	51.3	51	52.5	34.251
14	4	2	3	1	4	21.5	18	20	25.878
15	4	3	2	4	1	23	24	24.3	27.512
16	4	4	1	3	2	31.7	30	28	29.480

Table 4
Response for the Taguchi analysis of cyclooctene oxidation data.

Parameter	Mean S/N ratio			
	Level 1	Level 2	Level 3	Level 4
A. Imidazol (μmol)	22.057	30.384	32.313	29.280
B. $NaHCO_3$ (mmol)	30.152	24.332	32.017	27.534
C. Solvent	30.332	21.551	28.223	33.928
D. H_2O_2 (mmol)	26.456	23.383	31.539	32.656
E. Time (h)	26.043	24.830	31.542	31.620

Table 5
Analysis of variance.

Factor	DOF (*f*)	Sum of sqrs. (*S*)	Variance (*V*)	Percent (%*P*)
A	3	240.837	80.279	22.286
B	3	133.584	44.528	12.361
C	3	324.750	108.250	30.051
D	3	227.465	75.821	21.049
E	3	153.99	51.330	14.250
Other/error	0			
Total	15	1080.628		100.00%

array of L16 type was used, and is represented in Table 3. L and 16 mean Latin square and the replication number of the experiment, respectively. Five–four level factors can be positioned in an L16 orthogonal array table. The number in table indicates the levels of a factor [37]. The structure of Taguchi's L16 design and the results of measurement are shown in Table 3.

In the Taguchi method, the terms 'signal' and 'noise' represent the desirable and undesirable values for the output characteristic, respectively. The Taguchi method uses the S/N ratio to measure the quality characteristic deviating from the desired value. The S/N ratios are different according to the type of characteristic. In the case where bigger characteristics are

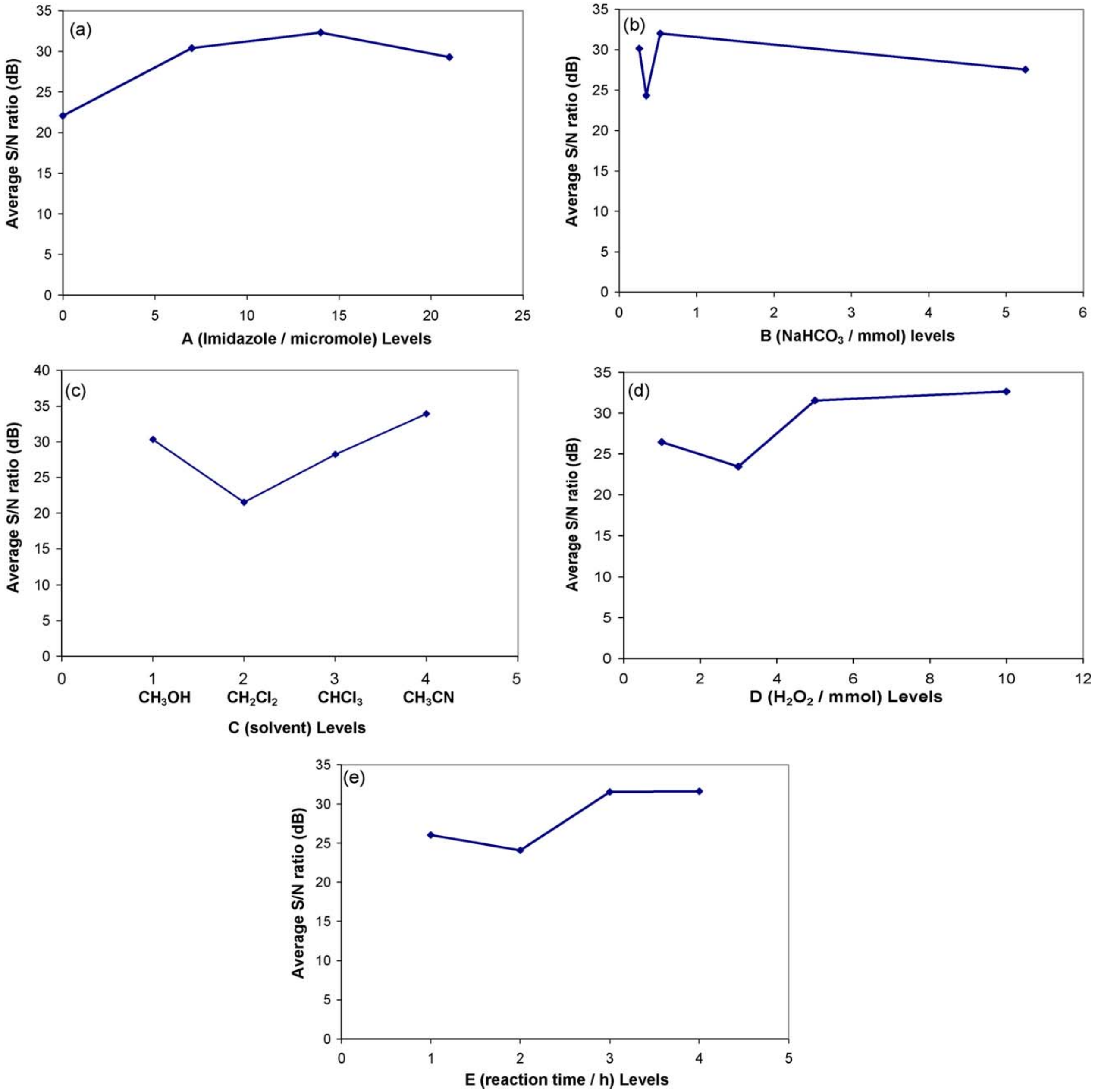


Fig. 2. Average S/N ratio for different levels of the parameters in oxidation of cyclooctene by Mn(TPP)OAc/Im/$NaHCO_3$ system: (a) imidazole, (b) $NaHCO_3$, (c) solvent, (d) H_2O_2, and (e) reaction time. See Table 2 for parameters and their values corresponding to their levels to be studied in the experiments.

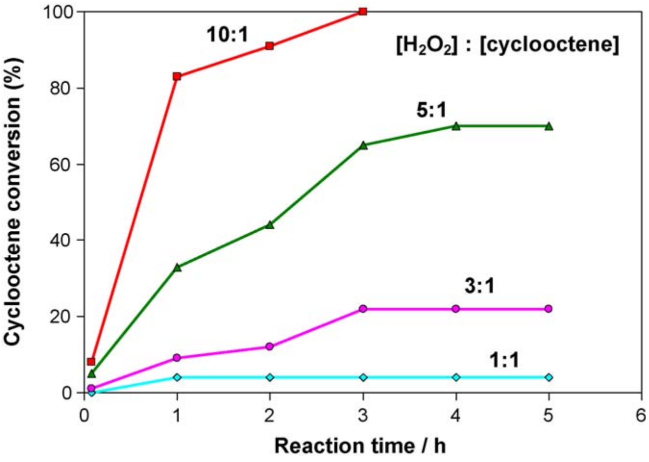


Fig. 3. Effect of hydrogen peroxide concentration on the oxidation of cyclooctene by Mn(TPP)OAc to the epoxide. *Reaction conditions*: cyclooctene (1 mmol), Mn(TPP)OAc (1.4×10^{-3} mmol), imidazol (1.4×10^{-2} mmol), $NaHCO_3$ (0.50 mmol), CH_3CN (3 mmol) and room temperature (27 ± 1 °C).

better, the S/N ratio is defined as [37]

$$\mathrm{S/N} = -10\log\left(\frac{1/y_1^2 + 1/y_2^2 + 1/y_3^2 + \cdots + 1/y_n^2}{n}\right) \tag{2}$$

where y_i is the characteristic property, n is the replication number of the experiment. The unit of S/N ratio is decibel (dB), which is frequently used in communication engineering. Table 3 shows the S/N ratio for the oxidation of cyclooctene calculated using Eq. (2). The mean S/N ratio for each level of the parameters was summarized as S/N response, which was shown in Table 4. Fig. 2 shows the average S/N ratio graph for oxidation of cyclooctene. Therefore, the optimum condition is A3, B3, C4, D4 and E4. In other words, based on the S/N ratio, the optimal parameters (conditions) for 1 mmol cyclooctene oxidation are A (imidazole) at level 3 (14 μmol), B ($NaHCO_3$) at level 3 (0.53 mmol), C (solvent) at level 4 (CH_3CN), D (H_2O_2) at level 4 (10 mmol) and E (time) at level 4 (4 h). Finally, in this case 100% epoxide yield can be obtained. This epoxide yield was confirmed twice by oxidation of cyclooctene with the obtained optimum conditions. In order to conduct an analysis of the relative importance of each factor more systematically, an analysis of variance (ANOVA) was applied to the data [36]. The main objective

Table 6
Oxidation of various olefins catalyzed by $Mn(TPP)OAc/Im/NaHCO_3/H_2O_2$[a].

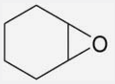
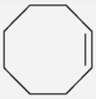
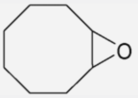
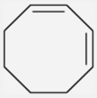
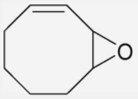
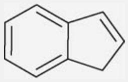
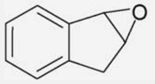
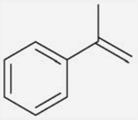
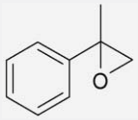
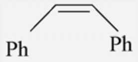
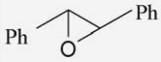
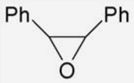
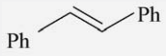
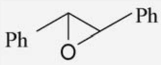
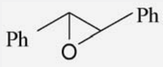
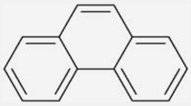
No.	Alkene	Product(s)[b]	Epoxide yield (%)[c]	Conversion (%)[c]
1			85	85
2			100	100
3			86	98.5
4			100	100
5			80	80
6			93	93
7			40[d]	71
			31[d]	
8			18[d]	18

Table 6 (*Continued*)

No.	Alkene	Product(s)[b]	Epoxide yield (%)[c]	Conversion (%)[c]
9			26	26
10	1-Octene	1-Octene oxide	26	26
11	1-Decene	1-Decene oxide	40	40

[a] *Reaction conditions*: Mn(TPP)OAc (1 mg, 1.376 μmol), Imidazole (14 μmol), $NaHCO_3$ (0.53 mmol) olefin (1.0 mmol), acetonitrile (3 ml), H_2O_2 (10 mmol), reaction time (4 h) and reaction temperature (25 ± 1 °C). Conversions and yields are based on the starting substrate.

[b] All products were identified by comparison of their physical and spectral data with those of authentic samples.

[c] Epoxide yield and conversion with respect to olefin.

[d] Yields determined by ^1H NMR.

of ANOVA is to extract from the results how much variation each factor causes relative to the total variation observed in the result. From the results of ANOVA in Table 5, the solvent had the largest percent (30.051%). The axial ligand imidazole (22.286%) and hydrogen peroxide (21.049%) indicated the second and third, respectively. Consequently, it can be concluded that the most influential factor was in the order of the solvent. $NaHCO_3$ had the least influence on the oxidation reaction. On the other hand, the degree of freedom (DOF) for each factor was 3 and total DOF was 15, so the DOF for error term was 0, and finally the variance for the error term (*V*e), obtained by calculating error sum of squares and dividing by error degrees of freedom, could not be calculated. Henceforth, it was impossible to calculate the *F*-ratio, defined as the variance of each factor dividing by *V*e. In order to eliminate the zero DOF from the error term, a pooled ANOVA was applied. The process of ignoring a factor once it was deemed insignificant was called pooling.

As confirming the results of the optimization of effective parameters using the Taguchi method, one factor, namely, the influence of reaction time on cyclooctene conversion at different $[H_2O_2]$/[cyclooctene] molar ratios was studied with the continuous variation method. The highest conversion of cyclooctene was achieved when the $[H_2O_2]$/[cyclooctene] molar ratios was 10:1 (Fig. 3). This finding is in complete agreement with the result of the Taguchi method and confirmed it.

3.3. Oxidation of various olefins

The applicability of the catalyst system was demonstrated in the epoxidation of a number of representative olefins under the same reaction conditions which proved to be the best for cyclooctene (Table 6). Cyclic olefins were transformed in excellent yield (80–100%) and selectivity (87–100%) (Table 6, run nos. 1–5). Electron-rich olefins displayed a greater reactivity than electron deficient olefins. The relatively electron-poor 1,3-cyclooctadiene shows lower reactivity than cyclooctene. This reflects the electrophilic nature of the oxygen transfer from the manganese–oxo [38] intermediate to the olefinic double bond. Allylic oxidation or formation of by-products, which is seen in the metalloporphyrin systems [39,40] was not observed in the epoxidation of alkenes such as cyclohexene. α-Methylstyrene was converted to the epoxide with 93% conversion in 4 h. This conversion is about two times faster than of its oxidation (50%) by HCO_3^-/H_2O_2 system in 24 h in acetonitrile [22]. In the epoxidation of *cis*- and *trans*-stilbene the steric effects are distinct. The sterically demanding *trans*-stilbene is less reactive than the *cis* isomer. Epoxidation of *trans*-stilbene proceeds with absolute stereospecificity. The oxygenation of *cis*-stilbene results in a *cis*- to *trans*-stilbene oxide ratio of 31:40. It was previously reported that the oxidation of *cis*-stilbene by Mn(TPP)Cl–PhIO, Mn(TPP)Cl–PhIO–Im and Mn(TPP)Cl–PhIO–pyridine systems giving 39:61, 93:7 and 57:43 mixture of *cis*- and *trans*-epoxides, respectively [41]. Typical epoxidizing reagents such as peroxyacids have been shown to react with *cis* olefins about two times faster than the corresponding *trans* olefin [42]. For *m*-chloroperoxybenzoic acid in methylene chloride at room temperature, *cis*- and *trans*-stilbenes are epoxidized at equal rates. This unequal reactivity was inferred to result from the nonbonded interactions between the phenyl groups of *trans*-stibene and the phenyl groups of Mn(TPP)OAc. A comparison of this catalytic system with previously reported [Mn(DCPP)]Cl/Im/benzoic acid/H_2O_2 systems shows that the conversion and the selectivity of *trans*-stilbene are higher than in the other systems [43]. The only product of the norbornene oxidation was *endo*-norbornene oxide. This result is in spite of the *exo*-epoxide from the oxidation of norbornene by HCO_3^-/H_2O_2 in CD_3CN/D_2O [22] and oxodiperoxo molybdenum(VI) complex $[MoO(O_2)_2(saloxH)]$ (saloxH$_2$ = salicylaldoxime)/$NaHCO_3/H_2O_2/CH_3CN$ [27] systems.

The Mn(TPP)OAc/Im/$NaHCO_3/H_2O_2$ system is active enough to oxidize even olefins with lowest activity like 1-octene and 1-decene (Table 6, nos. 10 and 11, with 100% selectivity) and cyclooctane to cyclooctanol (6%) and cyclooctanone (31%), not shown in Table 6. The activity of Mn(TPP)OAc/Im/$NaHCO_3/H_2O_2$ system is much higher than $HCO_3^-/H_2O_2/CD_3CN/D_2O$ [22] and $MnSO_4/NaHCO_3/H_2O_2/^tBuOH$ [24]

3.4. The catalyst anion and substrate concentration effects

To get insight into the role of the effects of catalyst anion and cyclooctene concentration on oxidation with two different catalytic systems, Mn(TPP)OAc/Im/$NaHCO_3/H_2O_2$ and Mn(TPP)Cl/Im/$NaHCO_3/H_2O_2$ were examined. The results of these studies (Table 7) revealed that the catalytic activity of Mn(TPP)OAc is better than that of Mn(TPP)Cl and with the Mn(TPP)OAc/Im/$NaHCO_3/H_2O_2$ system, the turnover number 4286 was obtained after 2 h. The less reactivity of Mn(TPP)Cl relative to that of Mn(TPP)OAc is

Table 7
Effects of catalyst anion nature and cyclooctene concentration on the reactivity of catalyst/imidazole/$NaHCO_3/H_2O_2$ system[a].

Cyclooctene	Catalyst (mmol)	Epoxide yield (%)	Reaction time (h)	TON[b]
Mn(TPP)OAc	1	100	3	714
Mn(TPP)OAc	2	86	5	1229
Mn(TPP)OAc	5	85	5	3036
Mn(TPP)OAc	10	60 (65)[c]	2 (5)	4286 (4643)[c]
Mn(TPP)Cl	1	93 (100)[c]	3 (5)	664
Mn(TPP)Cl	2	87	5	1243
Mn(TPP)Cl	10	67 (67)[b]	2 (5)	4786

[a] *Reaction conditions*: catalyst (1.4 μmol), CH_3CN (3 ml), Im (14 μmol), $NaHCO_3$ (0.53 mmol), H_2O_2 (5.0 mmol), reaction time (5 h) at room temperature.

[b] Turnover number = [epoxide]/[catalyst]. Yields based on starting cyclooctene.

[c] The results in parenthesis correspond to the results after 5 h.

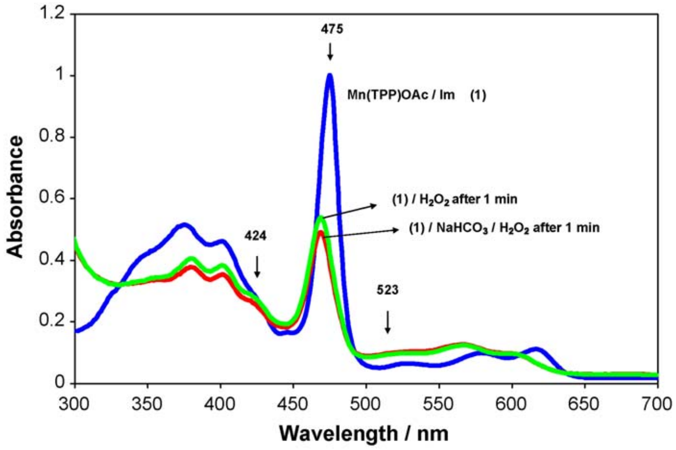


Fig. 4. The visible spectrum of the intermediate formed upon addition of H_2O_2 (0.21 M) to a solution of Mn(TPP)OAc (2.8×10^{-5} M), imidazole (6.99×10^{-6} M) and $NaHCO_3$ (1.0×10^{-2} M) in the UV–vis cell. Blue, Mn(TPP)OAc/Im (**1**); green, Mn(TPP)OAc/Im/H_2O_2 after 1 min; red, Mn(TPP)OAc/Im/$NaHCO_3$/H_2O_2 after 1 min.

probably due to the weak basicity of the chloride ion relative to that of the acetate counter ion.

3.5. Evidence for the formation of reactive intermediate

Clearly, the Mn(TPP)OAc complex generates active species upon reaction with H_2O_2/Im/$NaHCO_3$, because Mn(TPP)OAc/Im/$NaHCO_3$ can participate in efficient epoxidation as described above. The characteristics of stilbene oxidation by the Mn(TPP)OAc/Im/$NaHCO_3$/H_2O_2 system are very similar to those of the PhIO–Mn(TPP)Cl–imidazole system [41]: *cis*-stilbene is more reactive than *trans*-stilbene and gives the *cis*-epoxide predominantly. The only product of the oxidation of norbornene is *endo*-epoxide. The epoxidation of norbornene by *m*-chloroperbenzoic acid proceeds almost exclusively *exo* [44], whereas the formation of *exo*-norbornene oxide and *endo*-norbornene oxide in low *exo/endo* ratio has been reported with iodosylarenes using several substituted tetraphenylporphyrin and teterapyridylporphyrin iron(III) salts as catalysts [45]. It is concluded that the active oxygenizing species does not occur directly by the species resulted from H_2O_2–$NaHCO_3$.

The addition of H_2O_2 to a CH_3CN solution of Mn(TPP)OAc/Im/$NaHCO_3$/cyclooctene leads to the immediate appearance of a new species, characterized by peaks at 424 and 523 nm in the visible spectrum (Fig. 4). The spectrum is identical to that of H_2O_2/Mn(TPP)OAc/Im/cyclooctene. Although, the oxidation results show that $NaHCO_3$ dramatically affects the activation of H_2O_2 by Mn(TPP)OAc/Im, the similar characteristics of the Mn(TPP)OAc–H_2O_2–$NaHCO_3$–Im and Mn(TPP)Cl–PhIO-systems suggest a common active species. This species is very similar to that formed upon the reaction of PhIO with Mn(TPP)Cl which has been described as a high-valent Mn–oxo complex [38].

The lack of similar oxidizing ability, however, in the oxidation of cyclooctene with the Mn(TPP)OAc/Im/H_2O_2 system suggests that the effect of $NaHCO_3$ is at least in part due to its stabilizing effect on H_2O_2. The effect of sodium bicarbonate on the oxidation with hydrogen peroxide is like the effects of organic acids. As known, enhancement of the activity by acetic acid in the oxidation of cyclohexane has been reported in the literature [46,47]. In the medium of acetic acid, hydrogen peroxide is more stable and diminishes the self-decomposition by forming peroxyacetic acid. Activation of hydrogen peroxide by citric acid in acidic solution has been reported in [48,49]. It is proposed that the formation of peroxycitric acid is just like the formation of peroxyacetic acid.

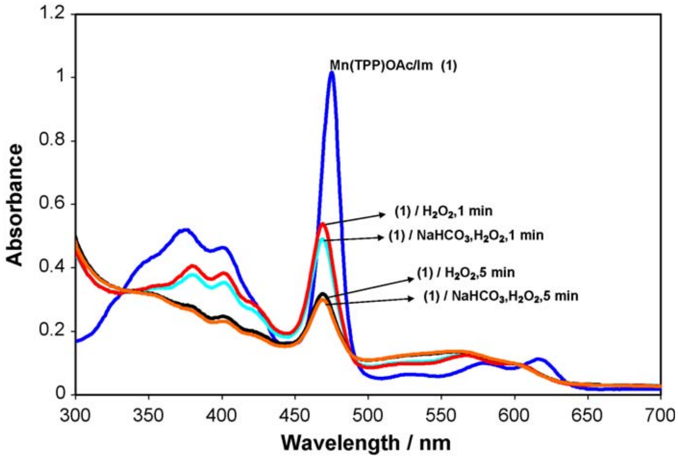
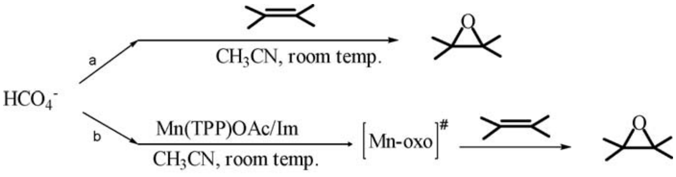


Fig. 5. The visible spectrum of Mn(TPP)OAc/Im, Mn(TPP)OAc/Im/H_2O_2 and Mn(TPP)OAc/Im/$NaHCO_3$/H_2O_2 after 1 and 5 min. Conditions as in Fig. 4.



Scheme 1. Two possible reaction pathways for the epoxidation of olefins by Mn(TPP)OAc/Im/$NaHCO_3$/H_2O_2 system: (a) direct oxidation of olefin by HCO_4^-, or (b) oxidation of olefin by the active species [Mn–oxo]$^\#$ which is formed *in situ* by the reaction of HCO_4^- and Mn(TPP)OAc/Im.

The reactivity of Mn(TPP)OAc/Im/$NaHCO_3$/H_2O_2 system is more than that of Mn(TPP)OAc/Im/H_2O_2 (Table 1). This finding was also confirmed by the faster reduction of Mn(TPP)OAc/Im Soret band in the presence of $NaHCO_3$/H_2O_2 relative to that of Mn(TPP)OAc/Im/H_2O_2 after 1 min (Fig. 5). Carboxylic acids and nitrogen-containing additives are considered to facilitate the heterolytic cleavage of the O–O bond in the manganese hydroperoxy intermediate, resulting in a catalytically active manganese(V)–oxo intermediate [43]. Drago et al. described the activating H_2O_2 by using the bicarbonate ion in their study of the oxidation of chemical warfare agents and sulfides in mixed *tert*-butyl alcohol/water solvent [50]. They concluded on the basis of NMR evidence that the active oxidant in the catalytic pathway is peroxymonocarbonate ion (HCO_4^-) formed by a labile preequilibrium reaction between bicarbonate ion and H_2O_2 (Eq. (3)).

$$HCO_3^- + H_2O_2 \rightleftharpoons HCO_4^- + H_2O \qquad (3)$$

We may summarize our findings as Scheme 1. The active species in the olefin oxidation with Mn(TPP)OAc/Im/$NaHCO_3$/H_2O_2 system is [Mn–oxo]$^\#$ which is formed by the reaction of HCO_4^- and Mn(TPP)OAc. This active species oxidizes olefins to the corresponding epoxides. Since the oxidation of norbonene was *endo*-epoxide, so the oxidation proceeds mainly by route b in Scheme 1.

4. Conclusion

The activation of C=C bonds of olefins and C–H bonds of alkanes can be achieved by the Mn(TPP)OAc/Im/$NaHCO_3$ system and hydrogen peroxide as the clean oxidant. The Taguchi method of system optimization was used to determine the optimized conditions and the percent of contribution (%*P*) of each factor. It was found that the solvent had the most influence on the oxidation and the imidazole amount stood in second place (22.286%). The

Mn^{III}-porphyrin in the presence of bicarbonate gives remarkably excellent selectivity and yield for the epoxidation of cyclic and linear olefins with H_2O_2. Sodium bicarbonate by stabilizing H_2O_2 prevents its fast decomposition and promotes its heterolytic cleavage for selective epoxidation. The bicarbonate-activated oxidation system is a simple, inexpensive, and relatively nontoxic alternative to other oxidants and peroxyacids, and it can be used in a variety of oxidations where a mild, neutral pH oxidant is required. The components of the system are inexpensive and environmentally friendly. The oxidation with Mn(TPP)OAc/Im/$NaHCO_3$/H_2O_2 proceeds by the mediation of Mn–oxo species.

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