INFLUENCE OF NITROGEN BASES ON EPOXIDATION OF CYCLOOCTENE WITH SODIUM PERIODATE CATALYSED BY MANGANESE(III) PORPHYRINS

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ABSTRACT: *Effects of imidazoles and substituted pyridines and pure σ−donors on the oxidation of cyclooctene with $NaIO_4$ by 5,10,15,20-tetraphenylporphyrinato-manganese(III) acetate, Mn(TPP)OAc, and 5,10,15,20-tetramesitylporphyrinato-manganese(III) acetate, Mn(TMP)OAc, catalysts in CH_2Cl_2-H_2O solvent are studied. Coordination of the nitrogen donors to the Mn-catalysts generally caused a reduction in the epoxidation rates, and an increase in their stabilities toward oxidative degradation. Steric properties of the donors rather than their basicity seems to be more dominating in these oxygenation reaction. The bulky Mn(TMP)OAc showed a greater steric sensitivity than Mn(TPP)OAc.*

KEY WORDS: *Epoxidation, Periodate, Manganese porphyrin, Nitrogen donors.*

The reactivities of hemoproteins such as cytochrome P-450, hemoglobin, and myoglobin, with protoheme IX as their common prosthetic group, are partly defined by the nature of the fifth ligand coordinated to the heme iron site [1]. Synthetic metalloporphyrins, in association with various oxidants, present good model systems to mimic the enzymatic role of cytochrome P-450 in the oxygenation of a variety of hydrocarbons [2]. Mn(TPP)Cl is an efficient catalyst in epoxidation of olefins with periodate in the presence of imidazole [3]. Herein we wish to report our results concerning the influence of several nitrogen bases, with different electronic and steric properties, on the epoxidation of cyclooctene by sodium periodate/manganese porphyrins catalytic systems.

In a typical reaction, in a round bottomed flask (25 mL) equipped with a magnetic stirrer, 0.5 mmol of cyclooctene and 2 mL of dichloromethane were successively added to 0.006 mmol of the catalyst, then 0.06 mmol of nitrogen base, 0.06 mmol of tetrabutylammonium bromide, and $NaIO_4$ (1 mmol in 10 mL

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Table 1: Epoxidation of cyclooctene with sodium periodate catalyzed by Mn(TPP)OAc and Mn(TMP)OAc in the presence of different nitrogen bases*

Nitrogen Base	pK_a[@]	Conversion(%) [Mn(TPP)OAc]	Conversion(%) [Mn(TMP)OAc]
None	—	30(59)	21(70)
2,6-Dimethylpyridine	6.60	28(62)	23(72)
Imidazole	6.65	22(62)	10(53)
1-Methylimidazole	7.06	23(55)	18(68)
Pyridine	5.27	22(51)	2(18)
4-tert-Butylpyridine	5.99	25(52)	14(55)
Piperidine	11.12	17(56)	23(85)
Quinuclidine	10.60	15(59)	27(90)

** The molar ratio for catalyst: base: tetra-n-butylammonium bromide: substrate: oxidant is 1:10:10:83:167. Reactions were analyzed after 15 minutes. Data in parentheses correpsond to 90 minutes. pK_a values obtained from [6].*

of water) were added to this solution and the mixture was stirred for the required time at room temperature. Gas chromatographic analysis was performed on the organic phase withdrawn directly from the reaction mixture. The identity of products were determined by IR, ^1H NMR spectral data.

Table 1 shows the results of epoxidation of cyclooctene with $NaIO_4$ mediated by Mn(TPP)OAc and Mn(TMP)OAc complexes in the presence of various nitrogen donors in CH_2Cl_2-H_2O medium at room temperature.

Evaluation of the results of epoxidation of cyclooctene by Mn(TPP)OAc in the first 15 minutes of the reaction shows that this catalyst leads to the highest yield (30%) in the absence of an axial nitrogen donor. This observation clearly contrasts with the results of olefin epoxidation using the same catalyst with other oxidants [4, 5a]. In the presence of 2,6-dimethylpyridine, a very similar yield (28%) was achieved. Presumably this is due to the inefficient coordination of the nitrogen base to the Mn(TPP)-OAc, which is caused by the steric hindrances of the methyl groups adjacent to the donor site [5].

Addition of small amounts of strong σ-donors, i.e. quinuclidine and piperidine, to the reaction mixture resulted in a reduction in the activity of the catalytic system. The lowered epoxide yields under this condition may be explained by the effects of coordination of the donors to Mn(TPP)OAc. The resulting six-coordinate (B)Mn(TPP)OAc, B=nitrogen base, species is expected to be catalytically less active than the five coordinate Mn(TPP)OAc, with an open coordination site, easily available for the oxygenation reactions.

Based on the higher basicity of 1-methylimidazole than imidazole one may expect that the former causes a greater deactivation of Mn(TPP)OAc than the latter, through a better coordination to the Mn-center. However, the higher steric effects of 1-methylimidazole seem to be dominating and hindering its close approach to the Mn-center. The observed difference in the behavior of pyridine and 4-tert-butylpyridine can not be explained in terms of their relative basicity. Thus, it appears that somehow the steric interactions of the bulky tail of the stronger donor, 4-tert-butylpyridine, with the phenyl groups of Mn(TPP)OAc inhibits its effective coordination to the Mn-center, leading to a smaller lowering of the rate of the catalytic reaction.

Differences among the conversions for epoxidation of cyclooctene in the presence or absence of various bases, after 90 minutes, are much less pronounced than those of the corresponding reactions at the shorter time (15 min). These results may be

explained in terms of the greater stabilities of Mn(TPP)OAc achieved in the presence of different nitrogen donors. Obviously, the open site of the five coordinate Mn(TPP)OAc complex is prone to an easy oxidative attack and destruction by the active oxidizing species produced during the catalytic cycle. Indeed in the absence of a nitrogen donor complete degradation of Mn(TPP)OAc occurred within 90 minutes, and only 59% conversion was reached. Whereas epoxidation of cyclooctene in the presence of imidazole resulted in 100% conversion after 3 hours.

Results of oxidation of cyclooctene by different Mn(TPP)OAc-$NaIO_4$-Base systems clearly demonstrate the direct influence of both electronic and steric properties of the donors. In the presence of various nitrogen bases, sterically hindered Mn(TMP)-OAc showed the same general trend in the epoxidation of cyclooctene as was observed for Mn(TPP)-OAc. The only exception with Mn(TMP)OAc is due to the behavior of σ-donors, piperidine and quinuclidine, which accelerate the epoxidations, and as yet no reasonable explanation is conceivable for this observation. Mn(TMP)OAc similar to Mn(TPP)OAc gives the same epoxidation yields, in the presence or absence of 2,6-dimethylpyridine. Results corresponding to the related imidazole, 1-methylimidazole pair and also pyridine, 4-tert-butylpyridine clearly display the greater importance of steric effects in Mn(TMP)OAc system. Apparently, the greater coordination of imidazole and pyridine than the related 1-methylimidazole and 4-tert-butylpyridine to the Mn-center has caused a larger decrease in the reaction rates again. While complete conversion of cyclooctene to the corresponding epoxide with Mn(TMP)-OAc in the presence of imidazole took 3 hours, the same reaction required only 140 minutes in the absence of a nitrogen base.

It is noteworthy that the results of epoxidation with Mn(TMP)OAc in short times (15 min) and long times (90 min) are closely related, and show similar trends in terms of steric characteristics of the nitrogen bases. This feature which is due to the high stability of Mn(TMP)OAc, is in sharp contrast with Mn(TPP)OAc system.

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