Ammonium Acetate as a very Simple and Efficient Cocatalyst for Manganese Porphyrin-catalysed Oxygenation of Hydrocarbons by Hydrogen Peroxide

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A one-phase system using chloro[tetra(2,6-dichlorophenyl)porphyrinato]manganese(III) catalyst and ammonium acetate cocatalyst epoxidised alkenes by H_2O_2 with complete conversion in excellent yield and hydroxylated alkanes with yields of 45–87%; for most reactions this system gave better results than a previously described analogous system using imidazole cocatalyst.

Recently, many systems using iron or manganese porphyrins as catalysts and various oxygen atom donors have been shown to efficiently mimic cytochrome P450-dependent monooxygenases.[1] In order to build up systems useful for selective oxidation in organic chemistry, H_2O_2 appeared to be a particularly interesting oxygen atom donor as it is an inexpensive, readily available oxidant which should give H_2O as the only by-product. However, use of H_2O_2 in the presence of Fe^{III} or Mn^{III} porphyrins leads to several difficulties such as homolytic cleavage of its O–O bond forming ·OH, the great propensity of iron porphyrins to dismutate H_2O_2, and the easy destruction of metalloporphyrins by H_2O_2.[1] Therefore, only few metalloporphyrin-based systems have been found that can efficiently catalyse hydrocarbon monooxygenation by H_2O_2. Iron(III) porphyrins bearing many electron-withdrawing substituents catalyse alkene epoxidation by H_2O_2 in good yields, in the absence of any cocatalyst,[2] but they appear as ineffective catalysts for alkane hydroxylation by H_2O_2. On the contrary, several systems based on Mn^{III} porphyrins have been shown to be able to perform both alkene epoxidation and alkane hydroxylation by H_2O_2, provided that a cocatalyst is used to facilitate the heterolytic cleavage of the O–O bond of H_2O_2. Most of these systems use the robust catalyst Mn(TDCPP)Cl [H_2TDCPP = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin] and either a nitrogenous base like imidazole,[3] an imidazole and a carboxylic acid like benzoic acid,[4] or a soluble base and a tertiary amine *N*-oxide[5] as cocatalysts. All of these systems suffer from a progressive consumption of the cocatalyst (heterocyclic base) in the oxidizing medium and (or) from their relative complexity [simultaneous use of several cocatalysts and (or) phase transfer agents].

Here we show that ammonium acetate alone acts as a very efficient cocatalyst for the Mn(TDCPP)Cl-catalysed epoxidation of alkenes and hydroxylation of alkanes by H_2O_2 in a one-phase CH_2Cl_2–MeCN system. This cocatalyst afforded better results for hydrocarbon oxygenation by H_2O_2 than imidazole under identical conditions and was not consumed during the oxidations.

Slow addition of diluted H_2O_2 (3% in H_2O) to a cyclooctene : Mn(TDCPP)Cl : NH_4O_2CMe mixture (40:1:10) in CH_2Cl_2 : MeCN (1:1) led to cyclooctene epoxide in high yield (95% based on cyclooctene after addition of only 1 equiv. of H_2O_2) in less than 15 min. Under identical conditions but with imidazole instead of NH_4O_2CMe, 2 equiv. of H_2O_2 were necessary to obtain similar yields.

Other salts were compared with NH_4O_2CMe as cocatalysts for the epoxidation of cyclooctene under the conditions indicated in Table 1 (cyclooctene : H_2O_2 : Mn(TDCPP)Cl : cocatalyst molar ratio = 700:20:1:10). Other ammonium salts not containing a carboxylate anion, like NH_4Cl and NBu_4Cl, were completely inactive and carboxylic acid salts not containing an ammonium cation like sodium acetate and sodium laurate, gave markedly lower yields. Ammonium formate and benzoate were active cocatalysts but not as efficient as NH_4O_2CMe. From these data, since NH_4O_2CMe appeared to be a an especially simple and efficient cocatalyst, the properties of the Mn(TDCPP)Cl–NH_4O_2CMe–H_2O_2 system were studied on several alkenes and alkanes and

compared with those of the Mn(TDCPP)Cl–imidazole–H_2O_2 system[3] under identical conditions.

The epoxidation of various alkenes led to the corresponding epoxides with good to excellent yields (82–95%). Table 2 shows that the complete conversion of cyclooctene to its epoxide was obtained with only 1 equiv. of H_2O_2 and that for less reactive alkenes, 2–4 equiv. were necessary. The excellent yield observed for cyclohexene epoxidation with formation of only small amounts of allylic oxidation products as well as the high yield obtained for less reactive monosubstituted double bonds as in non-1-ene illustrate the efficiency of the Mn(TDCPP)Cl–NH_4O_2CMe–H_2O_2 system for alkene epoxidation. Stereospecific epoxidation of *cis*-stilbene was observed resulting in the formation of a 97:3 mixture of *cis*- and *trans*-epoxide. When imidazole was used instead of NH_4O_2CMe under identical conditions, more equivalents of H_2O_2 (2, 4, 4 and 5 instead of 1, 3, 2 and 4 respectively for cyclooctene, cyclohexene, non-1-ene and *cis*-stilbene) were necessary to obtain similar yields.

Interestingly, the Mn(TDCPP)Cl–NH_4O_2CMe–H_2O_2 system was also efficient for the oxidation of alkanes which are much less reactive substrates. For instance, cyclooctane was converted to cyclooctanol and cyclooctanone in a 40% and 12% yield (based on cyclooctane) after addition of only 2 equiv. of H_2O_2. Slightly lower yields (34 and 12%) were obtained with the Mn(TDCPP)Cl–imidazole–H_2O_2 system and only after addition of 5 equiv. of H_2O_2 (Table 2). Similar results were observed for the less reactive cyclohexane which was oxidized to cyclohexanol and cyclohexanone with relatively good yields (36 and 16% after addition of 4 equiv. of H_2O_2) in the presence of NH_4O_2CMe and with slightly lower yields (28 and 10% after addition of 6 equiv. of H_2O_2) in the presence of imidazole. When a large excess of alkane was used [alkane : H_2O_2 : Mn(TDCPP)Cl : NH_4O_2CMe = 700:20:1:10], good yields based on starting H_2O_2 were obtained for cyclooctane (87%) and cyclohexane (76%) oxidation. Even a very unreactive alkane such as heptane was oxidized with a reasonable yield (45%) and this yield was higher than that obtained with imidazole as cocatalyst under identical conditions (Table 3).

Table 1 Effects of various salts as cocatalysts for the Mn(TDCPP)Cl-catalysed epoxidation of cyclooctene by H_2O_2[a]

Cocatalyst	Epoxide yield (%)
NH_4O_2CMe	95
NH_4O_2CH	54
NH_4O_2CPh	87
NaO_2CMe	74
$NaO_2CC_{12}H_{25}$ (laurate)	66
NH_4Cl	0
NBu_4Cl	0
NBu_4O_2CMe	82

[a] *Conditions*: using an excess of alkene (*vs* H_2O_2); addition of H_2O_2 (30% in H_2O diluted 10-fold with MeCN, 20 equiv. relative to catalyst) to an alkene : cocatalyst : Mn(TDCPP)Cl mixture (700:10:1) in CH_2Cl_2 : MeCN (1:1). Yields based on starting H_2O_2 after 2 h at room temp. (yields unchanged after 24 h).

Table 2 Oxidation of alkenes and alkanes by H_2O_2 catalysed by Mn(TDCPP)Cl and either NH_4O_2CMe (C) or imidazole (I), under conversion conditions[a]

Substrate	Products	Cocatalyst	Equiv. of H_2O_2 necessary[b]	Yield (%)	Total yield (%)
Cyclooctene	Epoxide	C	1		95
		I	2		93
Cyclohexene[c]	Epoxide	C	3		85
		I	4		91
Non-1-ene	Epoxide	C	2		87
		I	4		87
cis-Stilbene	cis-Epoxide[d]	C	4		88
		I	5		94
Cyclooctane	ol[e]	C	2	40	52
	one			12	
	ol	I	5	34	46
	one			12	
Cyclohexane	ol	C	4	36	52
	one			16	
	ol	I	6	28	38
	one			10	

[a] *Conditions*: progressive addition of H_2O_2 (30% in H_2O diluted 10-fold in MeCN) over 2 h to a solution of substrate, NH_4O_2CMe and Mn(TDCPP)Cl (40:10:1) in CH_2Cl_2:MeCN (1:1); Mn(TDCPP)Cl (1 mmol dm³). Reactions were performed under anaerobic conditions in the case of cyclooctane and cyclohexane. Yields based on starting substrate. [b] Number of molar equivalents of H_2O_2 necessary for maximum conversion of substrate. [c] Cyclohex-2-en-1-ol and cyclohex-2-en-1-one were also formed with yields of 3 and 1%. [d] Small amounts of trans-stilbene oxide were also formed (3% yield). [e] Ol and one are used for cyclooctanol (or cyclohexanol) and cyclooctanone (or cyclohexanone) respectively.

Table 3 Mn(TDCPP)Cl-catalysed oxidation of alkanes by H_2O_2 in the presence of NH_4O_2CMe (C) or imidazole (I) using an excess of alkane vs. H_2O_2[a]

Substrate	Products	Cocatalyst	Yield (%)[b]	Total yield (%)
Cyclooctane	ol	C	57	87
	one		15	
	ol	I	40	54
	one		7	
Cyclohexane	ol	C	50	76
	one		13	
	ol	I	31	39
	one		4	
Heptane	ols[c]	C	25	45
	ones		10	
	ols	I	19	29
	ones		5	

[a] Conditions as in Table 1 except that for cyclohexane and cyclooctane oxidations were performed under anaerobic conditions (argon). [b] Yields based on starting H_2O_2; total yields calculated by assuming that 2 equiv. of H_2O_2 are necessary for ketone formation. [c] % regioisomers at positions 1, 2, 3 and 4 = 4:67:25:4.

Another major interest of the NH_4O_2CMe cocatalyst is its high stability in the oxidizing medium. We found that after all the oxidations described above, further additions of substrates, H_2O_2 and Mn(TDCPP)Cl (when necessary) led to similar yields and rates without the need for further addition of NH_4O_2CMe.

The aforementioned results show that it is now possible to perform the cytochrome P450-type oxidation chemistry previously described for various systems using H_2O_2, Mn(TDCPP)Cl and a cocatalyst with a very simple, inexpensive and oxidation-resistant cocatalyst, ammonium acetate.

This result opens interesting perspectives for the use of H_2O_2 as a practical oxidant, for instance for the enantioselective epoxidation of alkenes by chiral Mn-porphyrins (or salen complexes)[6] reported so far with PhIO, ClO⁻ or peracids as oxidants.

References

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