Highly selective epoxidation of alkenes and styrenes with H_2O_2 and manganese complexes of the cyclic triamine 1,4,7-trimethyl-1,4,7-triazacyclononane

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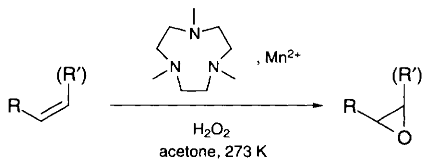
In acetone and at subambient temperatures, manganese complexes of 1,4,7-trimethyl-1,4,7-triazacyclononane catalyse the selective oxidation of many alkenes and styrenes to epoxides with an efficient use of H_2O_2; the regio- and chemo-selectivity resemble those of manganese–porphyrin catalysts.

Biomimetic oxidation catalysis has largely focused on complexes with planar tetradentate ligands such as manganese or iron porphyrins, or related macrocyclic *trans*-chelates.[1–3] Less is known about oxygen transfer from complexes with typical *cis*-coordinating ligands, such as bipyridine or cyclic triamines.[4] In the specific case of the interaction of non-planar manganese complexes with peroxides, undesired radical reactions or oxidant disproportionation often impede selective hydrocarbon functionalisation.[5,6] Manganese complexes of cyclic triamines were recently reported to catalyse styrene epoxidation in methanol–carbonate buffers.[7] Due to extensive oxidant decomposition, oxidant to substrate ratios of at least 100 were applied, which highly dilutes the substrate. We now report on the epoxidation properties of Mn in the presence of 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn). By choosing appropriate reaction conditions, the balance between epoxidation and peroxide disproportionation is strongly shifted towards the former, permitting the epoxidation of less reactive alkenes. Reactivity patterns of these manganese systems present surprising similarities to those observed for metal porphyrins.

Catalytic reactions (Scheme 1) were started by the gradual addition of aqueous, 30% H_2O_2, diluted in the organic solvent, to a mixture of alkenes/styrenes (1.0 mmol), solvent (0.6 g), Mn (1 µmol) and ligand (1.5 µmol).† Temperature and solvent strongly affect the epoxidation with Mn(tmtacn) (Table 1). In methanol, isopropyl alcohol or acetonitrile, only small amounts of the epoxide are obtained in a selective way. In the case of alcoholic solvents, solvent oxidation was proven to account at least partially for loss of oxidant. In all previous cases, gas bubbles developed rapidly when the oxidant was added without cooling, indicating that a major source of H_2O_2 loss is ≈ disproportionation to O_2. Such a gas evolution is hardly noticed in cold acetone, and a large increase of the catalyst turnover number is observed in these conditions. For styrene, a complete conversion with 98% epoxide selectivity is obtained with even <2 equiv. of oxidant. Analogous sharp increases of epoxide yields were observed for other alkenes, and the turnover numbers of up to 1000 compare favourably to those of polyoxometalate[8] or porphyrin-type catalysts.[1–3]

In the absence of tmtacn or Mn, no epoxidation is observed, even after prolonged reaction times (12 h). Replacing tmtacn with the non-methylated tacn results in a strong peroxide decomposition, without product formation. Epoxide yields are very dependent on the counter anion in solution. With sulfate and acetate, yields are *ca.* 4 times higher than with chloride or perchlorate salts. These differences are probably related to the known effects of these anions on the oxidative chemistry of Mn and tmtacn. Bridging anions such as sulfate and acetate are known to promote the formation of oxidized manganese dimers.[4] The occurrence of such dimers was confirmed by EPR spectroscopy: with sulfate and acetate, a strong 16-line signal of an $Mn^{III}Mn^{IV}$ dimer was observed, whereas with Cl^- and ClO_4^-, the 6-line signal of monomeric Mn^{II} is dominant.



Scheme 1

Table 1 Influence of solvent and temperature on oxidations with H_2O_2, catalysed by Mn(tmtacn)[a]

Substrate	Solvent	*T*/K	TO[b]	Selectivity (%)[c]
Cyclohexene	Buffered MeOH[d]	r.t.	39	90
	MeOH	r.t.	66	92
	Acetone	r.t.	290	87
	MeOH	273	37	91
	Acetone	273	890	89
Styrene	MeOH	r.t.	45	>98
	Acetone	r.t.	330	>98
	Acetone[e]	273	1000	>98
cis-Hex-2-ene	Acetone	273	540	>98
Hex-1-ene	Acetone	273	270	>98
E-β-Methylstyrene	Acetone	273	850	90
Cyclohexane	Acetone	273	9	Cyclohexanol
Hexan-2-ol	Acetone	273	400	Hexan-2-one

[a] *Conditions*: H_2O_2 (2 mmol, 30% in water, diluted 3 times in the organic solvent) is added over 1 h to a mixture of the alkene (1 mmol), tmtacn (1.5 µmol) and Mn^{2+} (1.0 µmol) in the organic solvent (0.6 g). Reactions were usually complete within 3 h; r.t. = room temperature. [b] Turnover number = (moles of substrate converted)/(moles of Mn). Maximum value is 1000 [see footnote (*a*)]. [c] Selectivity = (moles of epoxide)/(moles of substrate converted). For non-alkene substrates, the main product is given. [d] Methanol was mixed in a 1 : 2 ratio with a 0.2 mol dm^{-3} carbonate buffer at pH 9. [e] Only 1.5 equiv. of H_2O_2 was added.

In all cases, the epoxide is by far the favoured product. Cleavage of the double bond in styrenes, or allylic oxidation in the case of alkenes, are only minor side-reactions. With alkenes, the epoxide selectivity increases in the order *trans*-hept-3-ene (81%) < *trans*-hex-2-ene < cyclohexene < *cis*-hex-2-ene (>98%), reflecting that especially *cis* alkenes are smoothly epoxidized. Cyclohexene oxide or styrene oxide are stable under the reaction conditions. Retention of alkene configuration is not absolute, though the isomer scrambling is by far not as drastic as reported for some iron catalysts.[9] From *cis*-hept-3-ene for instance, a 77 : 23 mixture of the *cis* and *trans* epoxides is obtained, while the *trans*-alkene isomer yields a 9 : 91 *cis* : *trans* isomer ratio.

Competitive reactions show alkene reactivity to increase with the electron density of the double bond, *e.g.* allyl chloride < hex-1-ene < *cis*-hex-2-ene (Table 2). However, additional effects of alkene shape are obvious. First, *cis*-hex-2-ene gives about five time more epoxide than *trans*-hex-2-ene, which is only as reactive as the less substituted hex-1-ene. Secondly, 1-methylcyclohexene is far more reactive than cyclohexene in a peracid oxidation, but with Mn(tmtacn) and H_2O_2, the reactivity order is reversed. Finally, in the peracid oxidation of isoprene, the more electron-rich, methylated 1,2 double bond is largely preferred, but with the present catalytic system, an important shift of the regioselectivity towards the more exposed 3,4 bond is observed.

The reactivity of other substrate types was briefly investigated (Table 1). Alkanes such as cyclohexane are rather unreactive, but considerable ketone yields are obtained with secondary alcohols.

This catalytic system shows numerous similarities to the manganese porphyrin catalysts, as explored by Mansuy and coworkers.[1c] Many trends in chemo- and regio-selectivity (*e.g.* the preference for *cis*-alkenes) are the same, and comparable yields are obtained on substrate or H_2O_2 basis. In manganese porphyrin catalysis, imidazole or another axially binding cocatalyst is needed to allow an efficient H_2O_2 use. In Mn(tmtacn), either of the three nitrogen atoms is *trans* to any substitution-labile coordination site on Mn, which results in highly favourable yields on peroxide basis even in the absence of a cocatalyst. However, Mn(tmtacn) is distinct from manganese porphyrins because of a more pronounced alkene isomerisation, and the limited alkane oxidation. The strong dependence of the epoxide yields on reaction parameters such as temperature, solvent and anion probably results from a complex interplay between (*i*) competitive solvent oxidation, (*ii*) solvation of the partners in the catalytic reaction and (*iii*) metal speciation.

Table 2 Chemo- and regio-selectivity in alkene epoxidation with H_2O_2 and Mn(tmtacn)[a]

Alkene 1	Alkene 2	Epoxide 1/Epoxide 2[b]
Cyclohexene	Hex-1-ene	12.2
cis-Hex-2-ene	Hex-1-ene	5.2
trans-Hex-2-ene	Hex-1-ene	1.1
cis-Hex-2-ene	*trans*-Hex-2-ene	4.7[c] (1.3)
Allyl chloride	Hex-1-ene	0.14
Isoprene[d]		1.91 (4.9)
1-Methylcyclohexene	Cyclohexene	0.7 (8.7)

[a] *Conditions*: H_2O_2 (1 mmol), alkene 1 (0.5 mmol), alkene 2 (0.5 mmol), acetone, 273 K. [b] Values in parentheses were obtained through oxidation with MCPBA (273 K, CH_2Cl_2). [c] Calculated from the competitive reactions of the *cis*- and *trans*-alkenes with hex-1-ene. [d] 1,2-*vs.* 3,4-epoxide.

This work was supported by a grant from the US Department of Energy. D. D. V. is a post-doctoral researcher of NFWO (Belgium).

Footnote

† Product quantification was performed with GC–MS. Reference epoxides were synthesized by reaction with *m*-chloroperbenzoic acid (MCPBA) and identified by ^1H NMR spectroscopy. For the catalytic procedures: see Tables 1 and 2.

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Received, 30th November 1995; Com. 5/07815F