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Efficient Stereoselective Oxygenation of Alkanes by Peroxyacetic Acid or Hydrogen Peroxide and Acetic Acid Catalysed by a Manganese(IV) 1,4,7-Trimethyl-1,4,7-triazacyclononane Complex

John R. Lindsay Smith and Georgiy B. Shul'pin[1]

Department of Chemistry, University of York, York, Heslington, YO1 5DD, UK

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Abstract

The dinuclear manganese complex $[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$, where L is 1,4,7-trimethyl-1,4,7-triazacyclononane, catalyses the oxygenation of alkanes by peroxyacetic acid or by H_2O_2 in the presence of acetic acid to give alkanols, alkanones and alkyl hydroperoxides. The reactions can give large turnovers (up to 1350 after 1 h at 20 °C) and can occur with a high degree of retention of stereochemistry at tertiary carbon atoms. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Alkanes, Catalysis; Manganese and compounds; Oxygenations

The catalytic oxidation of unactivated aliphatic C-H bonds has been an active area of research for many years [1,2]. Recent attention has been focused on models for enzymic systems and on metal complexes that use cheap clean oxidants such as H_2O_2 or O_2 to bring about selective oxidation under mild conditions [2,3]. In this respect the recent report by Que and coworkers of stereospecific alkane hydroxylation by H_2O_2 catalysed by an iron(II) tri(2-pyridylmethyl)amine complex is of particular relevance [4]. Our interest in oxidations catalysed by manganese complexes of 1,4,7-trimethyl-1,4,7-triazacyclononane (TMACN) has led us to explore their potential in hydrocarbon oxidation [5].

The oxidation chemistry of manganese 1,4,7-triazacyclononane catalysts has developed very rapidly since the recent paper describing the use of the dinuclear manganese(IV) complex **1** as a catalyst for low temperature bleaching with H_2O_2 [6]. Subsequent studies have reported using **1** and related manganese complexes to catalyse the oxidation of alkenes, alcohols and phenols in both aqueous and organic solution [5,7-13]. We report here that **1** acts as an effective catalyst for alkane oxidation using either peroxyacetic acid or, more interestingly, H_2O_2 in the presence of acetic acid.

[1] Permanent address: N. N. Semenov Institute of Chemical Physics, Moscow 117977, Russia. E-mail: shulpin@center.chph.ras.ru or gb@shulpin.msk.ru. Fax: + (7095) 938 2156 or + (7095) 939 7417

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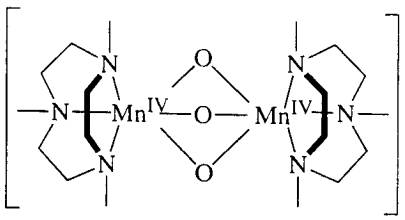

$(PF_6)_2$ (1)

Table 1

Oxidation of hydrocarbons by peroxyacetic acid in CH_3CN catalysed by complex **1** [a]

Substrates	Total TON [b]	Products	Yield/mmol dm^{-3} [c]
cyclohexane	485	cyclohexanone	76.6
		cyclohexanol	20.6
cyclohexane [d]	700	bromocyclohexane	139.0
		cyclohexanone	1.0
hexane	86	hexanones[e]	11.6
		hexanols[e]	5.6
methylcyclohexane	595	2-, 3- and 4-methylcyclohexanone[f]	59.0
		1-methylcyclohexanol	44.0
		2-, 3- and 4-methylcyclohexanol	14.0
cis-1,2-dimethylcyclohexane	470	*cis*-2,3- and 3,4-dimethylcyclohexanone	15.0
		cis-2,3- and 3,4-dimethylcyclohexanol	8.6
		cis-1,2-dimethylcyclohexanol	66.9
		trans-1,2-dimethylcyclohexanol	3.3
trans-1,2-dimethylcyclohexane	168	*trans*-2,3- and 3,4-dimethylcyclohexanone	15.9
		trans-2,3- and 3,4-dimethylcyclohexanol	6.7
		trans-1,2-dimethylcyclohexanol	10.0
		cis-1,2-dimethylcyclohexanol	0.9
adamantane [g]	306	adamantanone	0.07
		adamantanols[h]	61.2
cyclohexanol	1050	cyclohexanone	210.0

[a] Substrate, 0.4 mol dm^{-3}; peroxyacetic acid, 0.5 mol dm^{-3}; complex **1**, 0.2 mmol dm^{-3}; MeCN reaction volume 5 cm^3; 30°C; 1h; air. [b]Mols of all products per mol of the catalyst. [c]Product yields following treatment with PPh_3. [d] In the presence of $BrCCl_3$, 2.0 mol dm^{-3}. [e] 2- : 3-one = 71 : 29; 2- : 3-ol = 55 : 45. [f] 2- : 3- : 4-one = 25 : 55 : 20. [g]A suspension of the substrate, 2.0 mmol. [h] 1- : 2-ol = 95 :5.

The data (Table 1) show that **1** in acetonitrile is surprisingly effective at catalysing the rapid oxidation of alkanes by peroxyacetic acid. Both ketones and alcohols are obtained and alcohols, as expected [7,10], are oxidised to ketones. 3-Chloroperoxybenzoic acid can also be used but the oxidation yields are lower. In the absence of **1** negligible oxidation occurs in 1 h. GC analysis of the reaction mixtures, before and after treatment with PPh_3 [14], shows that alkyl hydroperoxides are formed in the initial stages of the oxidations and these are subsequently converted into alcohols and ketones. Examination of the regioselectivity of the oxidations reveals a small preference for reaction at C(2) over C(3) with hexane, and for C(3) and C(4) over C(2) with methylcyclohexane. The relative reactivity of the tertiary to secondary C-Hs in the methylcyclohexanes increases from 2 to 6 to 12 for the *trans*-1,2-dimethyl-, methyl- and *cis*-dimethyl-compounds respectively. The

oxygenations of *cis*- and *trans*-1,2-dimethylcyclohexane afford tertiary alcohols with a marked preference for retention of stereochemistry (RC_{cis} and RC_{trans} of 91 and 83%, respectively[1]).

Complex **1** also catalyses alkane oxygenations by *t*-BuOOH, PhIO and H_2O_2 in MeCN, although these reactions are much less efficient and occur without retention of configuration. Most interestingly, the oxidations by H_2O_2 in MeCN are accelerated dramatically by the presence of a carboxylic acid. Table 2 shows selected data for reactions in the presence of acetic acid. When the acetic acid is replaced by formic, propionic or trifluoroacetic acid or acetic anhydride the total turnover numbers (TON) for hexane oxidation are 0, 770, 345 and 400, respectively. The absence of hexane oxidation products from reactions in formic acid we believe arises from the latter acting as a reducing agent and competing effectively with hexane by trapping all the active oxidant.The alkane oxidations by the H_2O_2/HOAc/**1** system can also be carried out in acetone and less efficiently in methanol, however, no oxygenated products are obtained from reactions in pure acetic acid.

Table2

Oxidation of alkanes by H_2O_2 and acetic acid in CH_3CN catalysed by complex **1**[a]

Substrate	Total TON[b]	Products	Yields/mmol dm^{-3} [c]
hexane	1350[d]	hexanones[e]	155
		hexanols[e]	115
cyclohexane	640	cyclohexanone	51
		cyclohexanol	71
cyclohexane[f]	13	bromocyclohexane	2.6
		cyclohexanone	---
cycloheptane	850	cycloheptanone	70
		cycloheptanol	100

[a] Substrate,0.4 mol dm^{-3}; acetic acid, 1.0 mol dm^{-3}; H_2O_2, 0.5 mol dm^{-3}; complex **1**, 0.2 mmol dm^{-3}; alkane, 0.4 mol dm^{-3}; MeCN to give total volume 5 cm^3; 20 °C; 1 h. [b] Mols of products per mol of catalyst. [c] Product yields following treatment with PPh_3. [d] H_2O_2, 1.0 mol dm^{-3}. [e] 2- :3-ol = 57 : 43 and 2- : 3-one = 77 : 23. [f] In the presence of $BrCCl_3$, 0.1 mol dm^{-3}, 10 min.

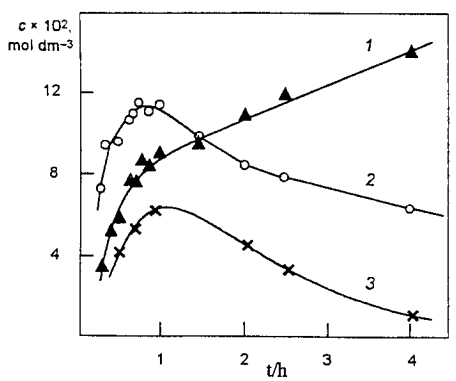

Fig 1 Oxidation of hexane (0.4 mol dm^{-3}) by H_2O_2 (0.5 mol dm^{-3}) in MeCN at 20 °C in the presence of CH_3COOH (1.0 mol dm^{-3}) catalysed by **1** (0.2 mmol dm^{-3}). Curves 1 and 2. hexanones and hexanols, respectively, measured after treatment with PPh_3. Curve 3, hexyl hydroperoxides obtained by comparison of chromatograms before and after treatment with PPh_3.

The time dependence of hexane oxidation (Fig. 1) shows that the reaction is biphasic; the first

[1] Parameter $RC_{cis} = 100(c_{cis} - c_{trans})/(c_{cis} + c_{trans})\%$; parameter $RC_{trans} = 100(c_{trans} - c_{cis})/(c_{trans} + c_{cis})\%$, where c_{cis} and c_{trans} are concentrations of *cis*- and *trans*-1,2-dimethylcyclohexanol, respectively

rapid phase, involving alkyl hydroperoxide formation, is complete in 1 h and is followed by a slow transformation of hydroperoxide into ketone. The oxidations of *cis*- and *trans*-1,2-dimethylcyclohexane give both tertiary hydroperoxides and alcohols with the measured stereoselectivity being greater before (RC_{trans} = 90%) than after (RC_{cis} = 54% and RC_{trans} = 66%) treatment with PPh_3.

Both the catalytic systems, with CH_3CO_3H and with H_2O_2/HOAc, have the characteristics of radical processes (some loss of stereochemistry, the formation of hydroperoxides and the formation of bromoalkanes from oxidations in the presence of the radical scavenger $BrCCl_3$). This conclusion is further supported by competitive oxidations of cyclopentane, cyclooctane and cyclododecane with cyclohexane which show that the relative reactivities of the substrates are similar although not identical to those obtained using O_2/H_2O_2/ hν, a system which is known to produce HO· radicals [15]. By analogy with Mn(III) porphyrin-catalysed alkane oxidations, the reactions catalysed by **1** can be rationalised by assuming the active oxidant is a manganese complex, possibly an O=Mn(V) species as suggested very recently by Barton *et al.* [13], which reacts by hydrogen atom abstraction in a solvent cage or via an 'oxygen-rebound' mechanism [16]: both these routes would afford products with retention of stereochemistry. Alkyl radicals, R·, that escape from the solvent cage react with dioxygen to generate ROO·, and subsequently ROOH with loss of stereochemistry. This accounts for the much greater stereoselectivity of the oxidation of 1,2-dimethylcyclohexanes by the H_2O_2/HOAc/**1** system prior to PPh_3 reduction. Since under the GC conditions the tertiary hydroperoxides are thermolysed to alkoxyl radicals that undergo fragmentation to ring-opened products and the only alcohol detected is that formed within the solvent cage or by oxygen-rebound.

Work is in progress to obtain definitive mechanistic information and to optimise these systems.

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