Hydrocarbon Oxidations with Hydrogen Peroxide Catalyzed by a Soluble Polymer-Bound Manganese(IV) Complex with 1,4,7-Triazacyclononane

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Dedicated to Prof. Roger Sheldon on the occasion of his 60th birthday.

Abstract: Soluble manganese(IV) complexes with polymer-bound 1,4,7-triazacyclononanes as ligands (compound **2**) catalyze the oxidation of alkanes by hydrogen peroxide in acetonitrile at room and lower temperatures. The corresponding alkyl hydroperoxides are the main products. The presence of a relatively small amount of acetic acid is obligatory for this reaction. The oxidation of alkanes and olefins exhibits some features (kinetic isotope effect, bond selectivities) that distinguish this system from an analogous one based on the dinuclear Mn(IV) complex **1**.

Keywords: alkanes; hydrogen peroxide; manganese complexes; olefins; oxidation

Introduction

Transition-metal complexes are capable of catalyzing hydrocarbon oxidations by molecular oxygen or/and various oxygen donors, particularly, hydrogen peroxide.[1–3] Manganese derivatives exhibit high activity in catalysis of oxidation of unsaturated and saturated hydrocarbons;[4] oxidations with participation of di- and polynuclear complexes of manganese are especially interesting.[5] High-valent manganese complexes with cyclic nitrogen-containing ligands are among these catalysts. Thus, manganese complexes with 1,4,7-triazacyclononane (TACN) and its derivatives, for example, with 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN) are known to catalyze oxidations of various organic compounds.[6] Manganese-containing enzymes as well as synthetic manganese-containing complexes are known to catalyze very efficiently the decomposition of hydrogen peroxide.[7] The photosynthetic water oxidation enzyme contains a polynuclear manganese core in the oxygen-evolving center (OEC).[8] Some examples of oxidations of organic compounds by hydrogen peroxide as well as by some other reagents are summarized in Table 1.[6] It can be seen that isolated and characterized complexes of manganese(IV) with TMTACN or similar N-containing ligands were used as catalysts for epoxidations of olefins and oxidations of benzyl alcohol or phenols by hydrogen peroxide.

It has recently been found that the dinuclear manganese(IV) complex [LMn^{IV}(O)$_3$Mn^{IV}L]$^{2+}$ (compound **1**), where L is TMTACN, used as the hexafluorophosphate salt, catalyzes oxygenation of some alkanes by H$_2$O$_2$ in the presence of carboxylic acids.[9] It is important to emphasize that no alkane oxidation occurs in the absence of carboxylic (usually acetic) acid. Higher alkanes (cyclohexane, n-pentane, n-heptane, methylbutane, 2- and 3-methylpentanes, 3-methylhexane, cis- and trans-decalins) were oxidized at 20 °C in acetonitrile (or nitromethane) solution to afford initially the corresponding alkyl hydroperoxides as the predominant products. Later in the course of the reaction these compounds decomposed to produce the corresponding ketones and alcohols. Turnover numbers (TONs) attained 3300 after 2 h, the yield of oxygenated products is 46% based on the alkane. Regio- and bond selectivities of the reaction are high: C(1):C(2):C(3):C(4) ≈ 1:40:35:35 and 1°:2°:3° is 1:(15 – 40):(180 – 300). The reaction with both isomers of decalin gave (after treatment with PPh$_3$) alcohols hydroxylated in the tertiary positions with the cis/trans ratio of ~2 in the case of cis-decalin, and the trans/cis ratio of ~30 in the case of trans-decalin. Light alkanes (methane, ethane, propane, normal butane, and isobutane) can be also easily oxidized by the same reagent in acetonitrile solution. The system "H$_2$O$_2$-compound **1**-MeCO$_2$H" also transforms secondary alcohols into the

Table 1. Systems based on Mn-TACN derivatives as catalysts for oxidations of organic compounds with hydrogen peroxide.[a]

Entry	Catalytic system	Reaction	Solvent	Ref.
Catalysis by individual Mn(IV) complexes				
1	Dinuclear Mn(IV) complexes with macrocyclic ligands	Bleaching of stains, epoxidation of 4-vinylbenzoic acid and styrene	Water	[6a]
2	Mn(IV) complex	Oxidation of 4-vinylbenzoic acid to the corresponding epoxide and styrylacetic acid to a mixture of the epoxide, diol and a ring-closed lactone	Water	[6b]
3	Dinuclear Mn(IV) complex with TMTACN	Oxidation of benzyl alcohols to benzaldehydes	Acetone	[6c]
4	Dinuclear Mn(IV) complex with TMTACN	Oxidation of phenols	Water	[6d, e]
5	Dinuclear Mn(IV) complex with TMTACN	Oxidation of sulfides to sulfones by periodic acid	Pyridine	[6f]
6	$[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$ (L = TACN derivative)	Epoxidation of styrene and dodecene	Two phase	[6g]
7	$[L^1Mn^{IV}_2(O)_3](ClO_4)_2$	Oxidation of lignin models		[6h]
8	$[L^*Mn^{III}(O)(AcO)_2Mn^{III}L^*](PF_6)_2$	Enantioselective epoxidation of olefins	Acetone	[6i]
9	$[TPTNMn_2(O)(OAc)_2](ClO_4)_2$	Epoxidation of olefins	Acetone	[6j]
10	$[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$ (L = TMTACN)-carboxylic acid	Hydroperoxidation of alkanes with partial retention of configuration	Acetonitrile or nitromethane	[9a−d]
11	$[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$ (L = TMTACN)-carboxylic acid	Epoxidation of olefins, oxidation of alcohols to ketones and sulfides to sulfoxides	Acetonitrile	[9d]
12	$[LMn^{IV}(O)_3Mn^{IV}L](PF_6)_2$ (L = TMTACN)-carboxylic acid	Oxidation of alkanes by *t*-BuOOH	Acetonitrile	[9d, e]
Catalysis by Mn complexes prepared in situ *from N-bases and Mn salts*				
13	TMTACN-$MnSO_4 \cdot H_2O$	Epoxidation of styrene and cyclohexene	Acetone	[6k]
14	A manganese faujasite containing TMTACN	Epoxidation of styrene and cyclohexene	Acetone	[6k]
15	TMTACN-Mn^{2+}	Epoxidation of olefins	Acetone	[6l]
16	TACN derivative-$MnSO_4.H_2O$	Epoxidation of olefins	Acetone or methanol	[6m]
17	Chiral TACN derivative-$Mn(OAc)_2 \cdot 4\,H_2O$	Enantioselective epoxidation of olefins	Methanol	[6n]
18	TACN covalently ancored on silica-$MnSO_4 \cdot H_2O$	Epoxidation of styrene and cyclohexene	Acetone or methanol	[6o]
19	Zeolite-exchanged Mn^{2+}-TMTACN	Oxidation of olefins and alkanes with H_2O_2 and *t*-BuOOH		[6p]
20	TMTACN-$MnSO_4 \cdot H_2O$-oxalic acid-Na oxalate	Epoxidation of olefins	Aqueous acetonitrile	[6q]
21	TACN derivative ancored on a solid-$MnSO_4 \cdot H_2O$	*cis*-Dihydroxylation and epoxidation of olefins	Acetonitrile	[6r]
22	TMTACN-$Mn(OAc)_2 \cdot 4\,H_2O$-sodium ascorbate	Epoxidation of olefins and oxidation of alcohols to ketones and carboxylic acid	Acetonitrile-water	[6s]
23	Polymer-bound TACN derivative-$Mn(OAc)_2 \cdot 4\,H_2O$-oxalic acid-sodium oxalate	Epoxidation of olefins and oxidation of alcohols	Acetone-methanol-water	[6t]

[a] L^1 is 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane; TPTN is *N,N,N',N'*-tetrakis(2-pyridylmethyl)propane-1,3-diamine.

corresponding ketones with quantitative yields at room temperature within a few minutes. Terminal aliphatic olefins such as hex-1-ene are quantitatively epoxidized by this system in acetonitrile at room temperature within 20 minutes. No epoxidation occurred in acetonitrile solution in the absence of acetic acid. Finally, dimethyl sulfide can be quantitatively and selectively converted into dimethyl sulfoxide within 3 h at room temperature.

Compound **1**
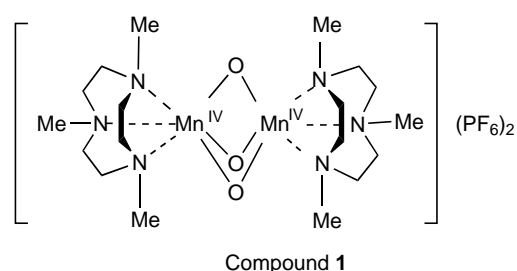
In some cases, complexes used as catalysts were not prepared synthetically but were formed *in situ* by mixing an *N*-containing ligand (usually TACN derivative) and a manganese(II) salt. Recently, it has been demonstrated that complexes formed *in situ* between polymers containing 1,4,7-triazacyclononanes (for example, compound **2**) and Mn(II) salts catalyze the epoxidation of simple olefins by hydrogen peroxide in aqueous acetone-methanol in the presence of sodium oxalate.[6t] Therefore, it was interesting to investigate the catalytic activity of a polymer-bound Mn(IV)-TACN derivative prepared from a polymeric ligand (compound **2**) in the alkane oxidation. Such a catalyst is relevant to compound **1**, which is (*vide supra*) active in acetonitrile only if acetic acid is present in a low concentration.
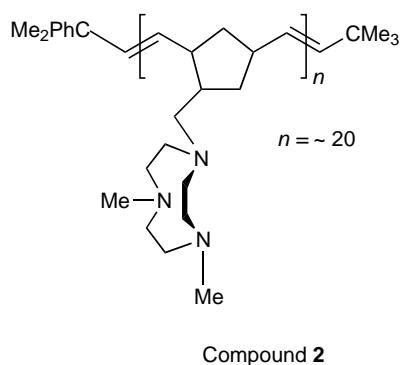
Compound **2**

Results and Discussion

As mentioned above, polymeric compound **2** in aqueous acetone−methanol solution forms a complex with $Mn(OAc)_2 \cdot 4 H_2O$ which catalyzes olefin epoxidation at $0\,^{\circ}C$ in the presence of oxalic buffer.[6t] Unfortunately, our attempts to perform the alkane oxidation under the standard conditions using acetonitrile as solvent remained unsuccessful due to the low solubility of **2** in this solvent. Previously we had found that catalysts prepared *in situ* from TMTACN and a manganese chloride were inactive in H_2O_2 oxidation of alkanes in acetonitrile.[9d] In contrast, a manganese(IV) derivative of polymeric compound **2** synthesized by a known procedure common for preparations of Mn(IV) complexes with macrocyclic *N*-ligands turned out to be capable of oxidizing saturated hydrocarbons. Thus stirring a homogeneous acetonitrile solution of the catalyst [which is a Mn(IV) complex of polymeric ligand **2**] with cyclohexane gave rise to the formation of the oxygenation products cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone as detected by GLC using a simple method proposed by some of us earlier.[2,10] The reactions were quenched by the addition of solid triphenylphosphine to the reaction solution, and GLC analysis gave concentrations of cyclohexanol and cyclohexanone. The comparison of the alcohol and ketone concentrations (measured by GLC) before and after the
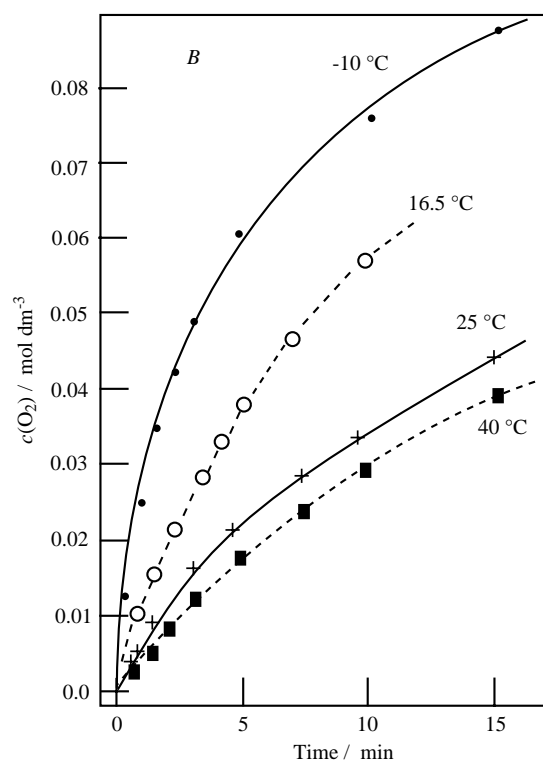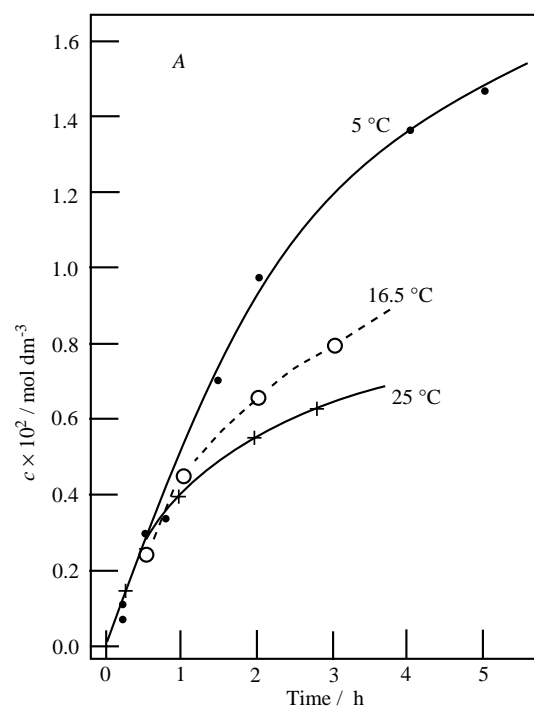
addition of PPh₃ testified that cyclohexyl hydroperoxide was formed as main product in the initial period. Indeed, the solution untreated with PPh₃ contained alkyl hydroperoxide, CyOOH, which completely or partially decomposed in GLC to produce CyOH, Cy=O, and other compounds. Added triphenylphosphine quantitatively reduced CyOOH to CyOH. The total concentration of cyclohexanol and cyclohexanone determined before treatment of the reaction sample with PPh₃ was usually somewhat lower than the concentration of the same products after the reduction with PPh₃. This difference can be easily understood, assuming either the partial decomposition of ROOH in the GLC to produce ring-opened products (e.g., adipic acid) or/and the appearance of a separate peak on the chromatogram for ROOH (in some cases we were able to detect such peaks). Due to this difference, for precise determination of oxygenate concentrations only data obtained after reduction of the reaction sample with PPh₃ were usually used, remembering, however, that the original reaction mixture contained of three products, cyclohexyl hydroperoxide (as predominant product), cyclohexanone, and cyclohexanol.

Figure 1 (graph *A*) shows that in the cyclohexane oxidation by the "H_2O_2-Mn(IV)-compound **2**-CH_3CO_2H" system the initial reaction rate does not depend on temperature. It is very interesting that the yield of the oxygenates after 1 hour is noticeably higher at low temperature. Total concentration of the oxygenates after 5 hours at $5\,^{\circ}C$ attains $0.015 \ mol \ dm^{-3}$. The alkane oxygenation is accompanied with the evolution of molecular oxygen. Curves for O_2 accumulation (calculated as concentrations $[O_2]$ in the reaction solution assuming conventionally that all O_2 is dissolved in acetonitrile) are shown in Figure 1 (graph *B*). It is noteworthy that the O_2 evolution is more rapid at low temperatures.
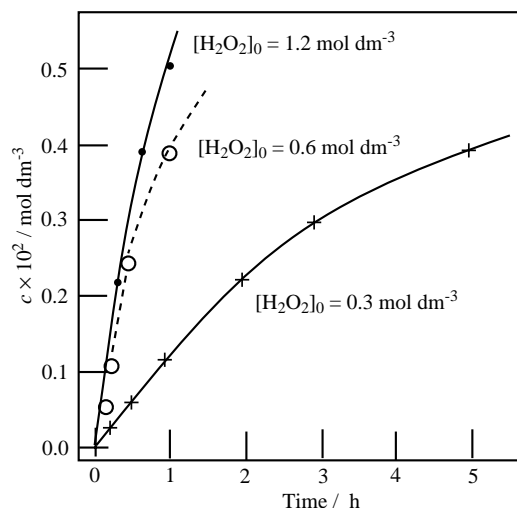
The oxidation rate and total product yield grow with increasing H_2O_2 concentration which is demonstrated by Figure 2. The reaction is of a first order with respect to the alkane concentration since the initial rate of the reaction is proportional to [cyclohexane] (Figure 3).

As for the case of catalysis by monomeric Mn(IV) complex **1**, the alkane oxidation with the "H_2O_2-Mn(IV)-compound **2**" system does not occur if acetic acid is absent. Figure 4 shows that the initial rate of the oxidation grows with increasing acetic acid concentration up to $0.5 \ mol \ dm^{-3}$. The system requires acetic acid also for the epoxidation of dec-1-ene (Figure 5). It should be, however, noted that, in contrast to the oxidation of terminal olefins with analogous system based on dimeric compound **1** as catalyst, the "H_2O_2-Mn(IV)-compound **2**-CH_3CO_2H" system is not very efficient since the epoxidation with 3-fold excess of H_2O_2 gives the epoxide in only 8% yield after 3 hours.
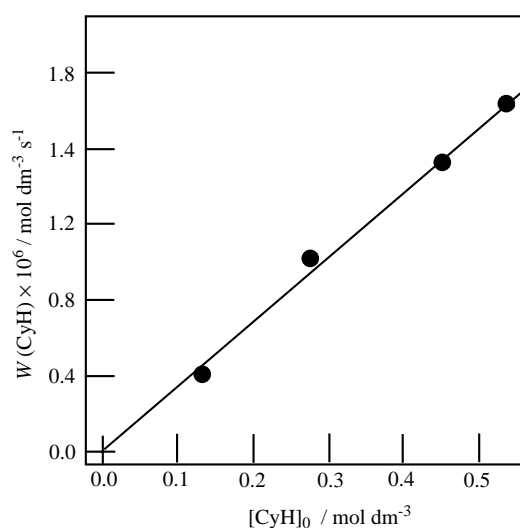
In order to get insight into the nature of the oxidizing species we determined selectivity parameters for the

Figure 2. Accumulation of cyclohexanol and cyclohexanone (total concentration, c) in cyclohexane (0.46 mol dm^{-3}) oxidation catalyzed by Mn(IV)-compound **2** catalyst (1.0 mg; volume of the reaction solution 1 mL) in the presence of acetic acid (0.25 mol dm^{-3}) at 25 °C at various initial hydrogen peroxide concentrations.

Figure 3. Initial rates of accumulation of cyclohexanol and cyclohexanone in cyclohexane oxidation catalyzed by Mn(IV)-compound **2** catalyst (1.0 mg; volume of the reaction solution 1 mL) in the presence of acetic acid (0.25 mol dm^{-3}) at 25 °C *versus* initial cyclohexane concentration.

Figure 1. Accumulation of cyclohexanol and cyclohexanone (total concentration, c) in cyclohexane (0.46 mol dm^{-3}) oxidation with H$_2$O$_2$ (0.6 mol dm^{-3}) catalyzed by Mn(IV)-compound **2** catalyst (1.0 mg; volume of the reaction solution 1 mL) in the presence of acetic acid (0.25 mol dm^{-3}) at various temperatures (graph A) and oxygen evolution by the same system [in the absence of cyclohexane; Mn(IV)-compound **2** catalyst, 1.5 mg; volume of the reaction solution 2.5 mL] at various temperatures (graph B).

alkane oxidations by the "H$_2$O$_2$-Mn(IV)-compound **2**-CH$_3$CO$_2$H" system and compared them with those obtained for some other systems. The oxidation of 2,2,4-trimethylpentane (isooctane) gave the two isomers of primary alcohols (after reduction of the reaction mixture with PPh$_3$) whereas the secondary and tertiary alcohols were only formed in minor quantities. For comparison, the oxidation of the same substrate with the "H$_2$O$_2$-compound **1**-CH$_3$CO$_2$H" in acetonitrile gave the
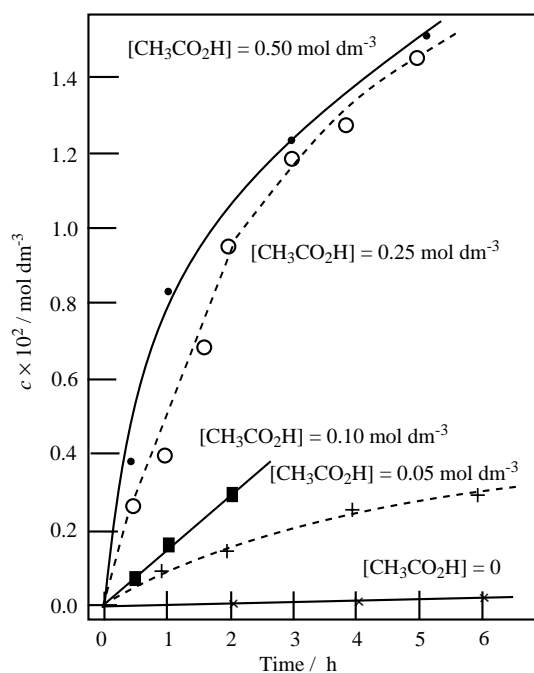
Figure 4. Accumulation of cyclohexanol and cyclohexanone (total concentration, c) in cyclohexane (0.46 mol dm^{-3}) oxidation with H_2O_2 (0.6 mol dm^{-3}) catalyzed by Mn(IV)-compound **2** catalyst (1.0 mg; volume of the reaction solution 1 mL) at $5\,°C$ at various acetic acid concentrations.
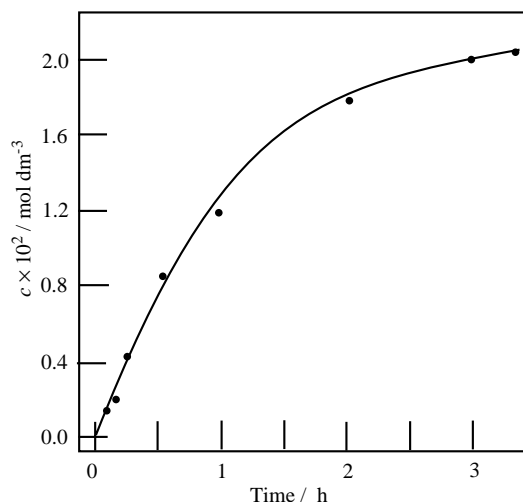
Figure 5. Accumulation of dec-1-ene epoxide (concentration, c) in dec-1-ene (0.26 mol dm^{-3}) oxidation with H_2O_2 (0.6 mol dm^{-3}) catalyzed by Mn(IV)-compound **2** catalyst (1.0 mg; volume of the reaction solution 1 mL) in the presence of acetic acid (0.25 mol dm^{-3}) at $3\,°C$.

selectivity parameter $1°:2°:3° = 1:5:55$ (here parameter $1°:2°:3°$ is normalized – i.e., calculated taking into account the number of hydrogen atoms at each carbon – relative reactivities of hydrogen atoms at primary, secondary and tertiary carbons, respectively). This parameter was found to be much lower ($1:2:6$, $1:3:6$

and $1:4:9$) for the hydroxyl radical-generating systems "O_2-H_2O_2-$h\nu$", "O_2-H_2O_2-$FeSO_4$" and "H_2O_2-VO_3^--PCA" (PCA is pyrazine-2-carboxylic acid), respectively. The oxidation of *cis*-decalin gave a mixture of *trans*- and *cis*-decalols in a ratio of $1.5:1$. Thus, this reaction proceeds non-stereoselectively. This is also in contrast to the oxidation with homogeneous dinuclear Mn(IV) catalyst **1** where this ratio was found to be 0.12. For the oxidations with the hydroxyl radical-generating systems mentioned above the same factors [*trans*-ol]/[*cis*-ol] were 1.3, 3.4, and 2.1, respectively. Finally, kinetic isotope effects ($KIE = k_H/k_D$) have been evaluated in the oxidations of cyclohexane and cyclohexane-d_{12} by the "H_2O_2-Mn(IV)-compound **2**-CH_3CO_2H" system in acetonitrile at 7 and $25\,°C$. At both temperatures the KIEs were 2.8. These values are noticeably higher than those determined for the corresponding oxidation with dinuclear complex **1** ($KIE = 1.3$).

Conclusion

Our first results described here show that like the analogous system based on dinuclear Mn(IV) complex **1**, the "H_2O_2-Mn(IV)-compound **2**-CH_3CO_2H" system oxidizes alkanes in acetonitrile solution to produce predominantly corresponding alkyl hydroperoxides. Both systems have in common that they require the presence of a carboxylic acid. In several aspects, however, they differ significantly. For example, in the oxidation of a branched alkane the bond selectivities are different and in decalin oxidations the stereoselectivity varies. Furthermore, the first system very efficiently epoxidizes terminal olefins, whereas the polymer-bound Mn(IV) complex is only a weak catalyst. Apparently, the two systems oxidize organic substrates *via* different mechanisms and additional studies shall reveal further insight into the details of the mechanistic pathways.

Experimental Section

Catalyst Preparation

The synthesis of **2** was carried out by polymerization of monomeric norbornene-*N*-substituted di-*N*-methylated 1,4,7-triazacyclononane as described previously.[6t] The Mn(IV) complex of this polymer-substituted 1,4,7-triazacyclononane was prepared using a procedure common for the preparation of such type compounds.[11] The polymeric 1,4,7-triazacyclononane (compound **2**; 96 mg; 0.35 mequiv.) was dissolved in 2 mL of a EtOH/H_2O ($2/1$ v/v) mixture. Then $MnCl_2 \cdot$ aq (44 mg, 0.35 mmol) and NH_4PF_6 (85.6 mg, 0.52 mmol) were added, and the mixture was stirred at $40\,°C$ for 20 minutes. The mixture was then cooled to $0\,°C$ and stirred at that temperature for 10 min. An aliquot of H_2O_2 (30% in H_2O, 0.035 mL, 0.35 mmol) was diluted up to 0.35 mL with water and mixed with NaOH (1.5 mol dm^{-3}; 0.35 mL). This solution was added

to the reaction mixture over 2–3 min (successive aliquots of 0.1 mL up to the total volume of 0.7 mL), and the resulting mixture was stirred for 15 min at 0 °C. After that H_2SO_4 (1 N; 0.1 mL) was added to the reaction solution. The mixture was diluted with CH_3CN and filtered through celite. The filtrate was evaporated to dryness, then redissolved in CH_3CN and filtered again to eliminate a white precipitate. After evaporation of the solvent, a red solid product was obtained (165 mg, corresponding to 95% yield).[6t]

Oxidation Experiments

Oxidation reactions were carried out in air in MeCN in thermostatted Pyrex vessels with vigorous stirring. The total volume of the reaction solution in each case is given in a figure caption. In order to determine concentrations of all possible cyclohexane oxidation products the samples of the reaction solutions were analyzed twice, before and after their treatment with PPh_3, by GLC measuring concentrations of cyclohexanol and cyclohexanone (instrument LKhM 80/6; column 2 m; 5% Carbowax on Inerton AW-HMDS). This very simple method proposed and described by some of us earlier[2,10] allows us both to detect alkyl hydroperoxides and to measure the real concentrations of alkyl hydroperoxide, alcohol, and aldehyde or ketone present in the reaction solution (usually alkyl hydroperoxides are decomposed in the gas chromatograph to produce mainly the corresponding ketone and alcohol).

Acknowledgements

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