Mild oxidation of alkanes and toluene by tert-butylhydroperoxide catalyzed by an homogeneous and immobilized Mn(salen) complex

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ABSTRACT

Mild oxidations with t-BuOOH of linear (n-pentane, n-hexane, n-heptane and n-octane) and cyclic (1,2-dimethylcyclohexane) alkanes to the corresponding secondary alcohols and ketones, as well as of toluene to benzaldehyde, catalyzed by homogeneous and immobilized Mn(salen) (on a polydimethyl-siloxane (PDMS) based membrane, Mn(salen)-PM) systems [Mn(salen) = {(R,R)-N,N-bis(3,5-di-tert-butylsalicylidenato)-1,2-cyclohexanediamine(2-)}chloro manganese(III)], have been studied. These oxidations are markedly promoted by the addition of various acids, namely nitric, pyrazine-2-carboxylic, acetic, benzoic and oxalic acids. Regio- and stereoselectivity parameters are dependent on the immobilization of the catalyst on the support and on the type of acid promoter, and correlate with the sorption values of alkane substrates on the PDMS membrane. The oxidation was shown to proceed with participation of t-BuO$^{\bullet}$ and alkylperoxyl (ROO$^{\bullet}$) radicals. The toluene oxidation systems feature a high selectivity towards the formation of benzaldehyde (mainly in the case of the supported catalyst) and remarkably high catalyst turnover numbers (up to 1.7×10^3).

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1. Introduction

The oxidative functionalization of alkanes to more valuable products (e.g. alcohols, ketones, aldehydes) is a subject of a high current attention [1–8]. Manganese and iron(III) complexes of porphyrins, tetraazaannulenes, phtalocyanines, chlorins, Schiff bases and triazacyclononanes have been extensively studied as alkane oxidation catalysts [1,9–17]. However, there are relatively few reports on alkane oxidations catalyzed by Mn(salen) complexes [salen = (R,R)-N,N-bis(3,5-di-tert-butylsalicylidenato)-1,2-cyclohexanediamine(2-)], which traditionally have been used mainly for epoxidation reactions [18–25]. With respect to alkanes, such systems have been applied to cycloalkanes oxidations, being based on Mn(salen) compounds that are (i) encapsulated in zeolite Y [26], (ii) covalently bound to a Keggin type polyoxometalate [27], or (iii) immobilized on an alumina matrix [28]. Reports on their use as catalysts for the oxidation of linear alkanes (i.e., n-heptane, n-octane, n-hexane and n-pentane) are even scarcer in the literature [29].

Low selectivity is an important and common problem of oxidative catalysis and therefore the preferential oxidation of one of the carbon atoms in an alkane molecule is a highly desirable task to achieve [1–3,7,30]. The regioselectivity (i.e., the preference of functionalization of certain positions in an alkane chain over all the other possible ones) and stereoselectivity (i.e., preferential formation of one stereoisomer over another) can be enhanced if the reaction centres are surrounded by bulky substituents or are placed into hydrophobic pockets [30]. For example, enzymes and biomimetic systems can induce regio- and stereoselective transformations of alkanes in such ways.

Membranes containing encapsulated metal catalysts have been designed to induce selectivity of the reaction due to the membrane affinity for different reagents. Polydimethylsiloxane (PDMS) is one of the supports that is very interesting from this point of view. Apart from being cheap and easy-to-prepare, this polymer, due to the presence of flexible siloxane chains, provides a fast mass transfer through the membrane. Furthermore, it creates an hydrophobic environment around the metal active site, thus leading to the control of the reactants sorption by preferential uptake of apolar molecules such as alkanes [31–35]. Thus, the hydrophobic PDMS membranes may act as reactants reservoir, enhancing the reaction selectivity and preventing the over-

oxidation of products, which due to the different hydrophobicity/hydrophilicity in comparison with the starting material, are forced to leave the catalytically active surface of the membrane. Therefore, depending on the chemical nature of membrane, it is possible to supply a supported catalyst in a special form that is more active and selective in comparison with the homogeneous one.

The PDMS-based membranes have been earlier used for the immobilization of metalloporphyrins [36], metallophtalocyanines [32,37] and Mn(salen) complexes [38,39]. The latter were further applied to catalyze efficiently oxidation reactions in the presence of t-BuOOH as oxidant. H_2O_2 is less efficient since the hydrophobic membrane creates a barrier against H_2O_2, thus preventing its sorption and subsequent reaction.

Following our continuous interest in the oxidation [40–59] and carboxylation [59–64] reactions of alkanes catalyzed by various Cu [40–46,64], V [47,61–63], Fe [37,49] and Re [51,52,60] compounds, the present work aims to extend these studies to a different metal (Mn) centre and to explore the application of the Mn(salen) complex {(R,R)-N,N-bis(3,5-di-tert-butylsalicylidenato)-1,2-cyclohexanediamine(2-)}chloro manganese(III), under both heterogeneous (immobilized on a PDMS-based membrane) and homogeneous conditions for the oxidation of linear and cyclic alkanes and toluene. The possible promoting selectivity effect of PDMS could thus also be tested for such reactions.

2. Experimental

2.1. Materials

The polymeric membranes were prepared by a polycondensation reaction between poly(dimethylsiloxane) (PDMS) and the alkoxide groups of pentaerythritholtriacrylate (PETA), 2-aminoethyl-3-aminopropyltrimethoxysilane (AS) and tetraethoxysilane (TEOS). The Mn(salen) complex was then encapsulated in the free volume of the PDMS polymeric network (Fig. 1), giving the heterogeneous catalyst Mn(salen)-PM. The synthetic procedure and full characterization of Mn(salen)-PM have already been reported [38]. All the chemicals were obtained from commercial sources and used as received.

2.2. Typical procedure for alkane and toluene oxidation reactions

A typical oxidation reaction was carried out under air as follows: the catalyst Mn(salen) (0.08 or 0.16 μmol), as a 0.2 mM stock solution in acetonitrile or immobilized on a polymeric membrane [Mn(salen)-PM], and co-catalyst [such as, nitric, pyrazine-2-carboxylic (PCA), acetic (AcOH), benzoic (PhCOOH) or oxalic (COOH)$_2$ acid], in the form of a 0.16 M stock solution in acetonitrile (2.4–7.2 μmol), were mixed in CH_3CN (3.0 mL) with vigorous stirring, followed by the addition of the substrate (alkane or toluene, 2.0 mmol) and an aqueous (70%) solution of tert-butyl hydroperoxide (5.0 mmol).

The reaction mixture was stirred for 4–24 h at room temperature and air atmospheric pressure. The product analysis was performed as follows: cycloheptanone (GC internal standard, 10 μL) was added to the final reaction solution; the obtained mixture was stirred during ca. 10 min, whereafter a small aliquot was taken and analyzed by gas chromatography (GC) using a Fisons Instruments model 8160 gas chromatograph equipped with a DB-WAX capillary column (column length: 30 m; internal diameter: 0.32 mm; film: 0.25 μm; helium was a carrier gas) and a FID detector. The products were identified by comparison of their retention times with those of authentic samples.

All samples were usually analyzed by GC twice before and/or after the addition of an excess of solid triphenylphosphine (PPh$_3$) in order to reduce the alkyl hydroperoxides (if present) to the corresponding alcohols, following the method developed by Shul'pin [65,66].

The performed blank experiments confirmed that no products of alkane or toluene oxidation were obtained unless the catalyst was added. The Mn(salen) free PDMS membrane was also shown to not catalyze the oxidation of alkanes and toluene.

Eventual leaching from the membrane of the supported Mn(salen) complex, in the presence of different solvents, was screened by UV–vis spectroscopy. In accord with a prior study [33], a slight Mn leaching was observed in the case of an apolar solvent (such as CH_2Cl_2), whereas it does not occur in the presence of a polar one (e.g. MeCN) due to the low membrane swelling. Moreover, in order to test the possible involvement of homogeneous Mn-species when the heterogeneous Mn(salen)-PM was used, the following experiment was performed. Mn(salen)-PM was mixed with acetonitrile and t-BuOOH under typical reaction conditions. After 1 h of intensive stirring, the Mn-containing membrane was removed, and n-heptane was added into this solution. After additional stirring during 5 h, the reaction solution was analyzed by GC. No traces of oxygenated products were observed, thus excluding the hypothesis of a significant involvement of an homogeneous route, and fully supporting the heterogeneous process.
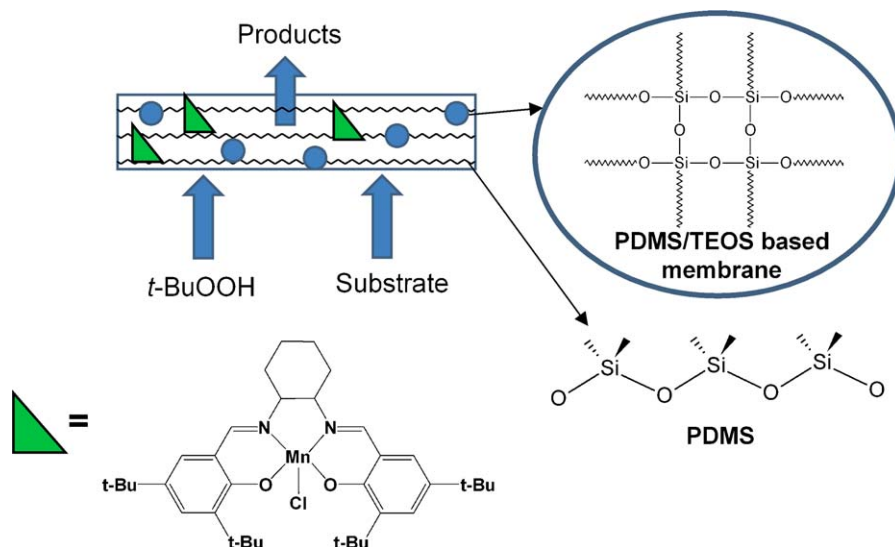

Fig. 1. Schematic representation of substrate (alkane and toluene) oxidations with a Mn(salen) complex encapsulated in a polymeric PDMS-based membrane.

Table 1
Oxidation of isomeric 1,2-dimethylcyclohexanes (DMCH) with *t*-BuOOH catalyzed by Mn(salen)-PM (immobilized on PDMS-based membrane) and Mn(salen)[a].

Entry	Catalyst	Additive	*cis/trans*[b]	
			cis-DMCH	*trans*-DMCH
1	Mn(salen)-PM	None	0.69	3.03
2	Mn(salen)	None	0.97	2.92
3	Mn(salen)-PM	HNO$_3$	1.07	1.18
4	Mn(salen)	HNO$_3$	1.89	1.04
5	Mn(salen)-PM	PCA	1.83	1.21
6	Mn(salen)	PCA	2.07	1.09
7	Mn(salen)-PM	AcOH	2.30	3.25
8	Mn(salen)	AcOH	2.71	2.21
9	Mn(salen)-PM	PhCOOH	2.52	3.49
10	Mn(salen)	PhCOOH	2.63	2.33
11	Mn(salen)-PM	(COOH)$_2$	2.91	4.51
12	Mn(salen)	(COOH)$_2$	5.43	2.65

[a] *Reaction conditions*: Catalyst (0.08 μmol), acid additive (2.4 μmol), substrate (2.0 mmol), oxidant *t*-BuOOH (5.0 mmol) in acetonitrile (3.0 mL), 24 h, r.t.
[b] Parameter *cis/trans* = [*cis*-ol]/[*trans*-ol], i.e. the ratio between concentrations of alcohol (1R,2R or 1S,2S)-1,2-dimethylcyclohexanol and (1R,2S or 1S,2R)-1,2-dimethylcyclohexanol stereoisomers (*cis*-ol and *trans*-ol) formed in the oxidation of *cis*- or *trans*-DMCH.

2.3. Sorption measurements

For the sorption measurements, the dried sheet-shaped Mn(salen)-PM samples were immersed in the liquid alkane (*n*-pentane, *n*-hexane, *n*-heptane and *n*-octane) at room temperature. After 24 h of immersion and the removal of the excess of liquid, the swollen membrane was weighted again. The sorption of alkanes on the membrane was obtained by determining their swelling using the following expression [67].

$$\text{Sorption (mmol g}^{-1}) = \frac{\{(W1 - W2)/W1\} \times 1000}{MW}$$

where $W1$ and $W2$ stand for the membranes weights (g) in the wet and dry states, respectively, and MW is the molecular weight of the alkane.

3. Results and discussion

3.1. Alkane oxidations

The catalytic activity of the polymeric membranes based on the poly(dimethylsiloxane) containing Mn(salen) complex was evaluated for the alkanes oxidations by *tert*-butylhydroperoxide (*t*-BuOOH) in acetonitrile solutions and in the presence of some additives. The obtained results were compared with those of the conventional homogeneous system, which was also investigated in this work.

Since the study of stereoisomers oxidation, such as *cis*- and *trans*-1,2-dimethylcyclohexane (DMCH), can provide information about the types of reaction mechanism and species involved [1–3,10,68], we have also included such alkanes within those we have selected for studying. While retention of the stereochemical configuration is characteristic of a concerted reaction mechanism (in enzymes, however, the retention can be imposed by the active site geometry), loss of the stereochemical configuration is indicative of a nonconcerted mechanism that involves an intermediate [1–3,30,68]. The results on the oxidation of *cis*-1,2-dimethylcyclohexane by Mn(salen) or Mn(salen)-PM in the presence of different additives, such as nitric, pyrazine-2-carboxylic (PCA), acetic (AcOH), benzoic (PhCOOH) and oxalic (COOH)$_2$ acids, are presented in Table 1 and Fig. 2. It was earlier found [1–3,40–44,47–49,52,53,59,65,66,69–76] that such acids may promote the oxidation of alkanes catalyzed by some transition metal compounds.

As a first general observation, one can mention that the stereochemical configuration is not retained, starting from either *cis*- or *trans*-1,2-dimethylcyclohexane, thus showing that the mechanism is nonconcerted in both cases.

As can be seen from Fig. 2a, without an acid additive the oxidation of *cis*-1,2-dimethylcyclohexane catalyzed by both Mn(salen) and Mn(salen)-PM is not stereoselective, since the *cis/trans* ratio is close to the unity. However, in the presence of an acid additive the oxidation proceeds in a stereoselective manner with the retention of *cis*-configuration, following the increase of the *cis/trans* ratio. The latter is dependent on the type of acid additive and follows an increasing trend: nitric < pyrazine-2-carboxylic < acetic ≤ benzoic < oxalic acid. The *cis/trans* ratio of 5.4 obtained in the presence of oxalic acid is close to that reported for the oxidation of alkanes with another Mn complex bearing 1,4,7-trimethyl-1,4,7-triazacyclononane in the presence of (COOH)$_2$ and H$_2$O$_2$ [76].

The oxidation of *trans*-1,2-dimethylcyclohexane is also not stereoselective in the presence of HNO$_3$ and PCA as additives (Fig. 3). However, reactions in the absence of any acid additive, as well as those promoted by AcOH, PhCOOH and (COOH)$_2$, lead to the inversion of configuration, with preferable formation of the *cis*-over the *trans*-isomer, and achieving the highest *cis/trans* ratio of 4.5 in the case of oxalic acid. Thus, the oxidation of both *trans*- and *cis*-1,2-dimethylcyclohexane leads preferably to the formation of
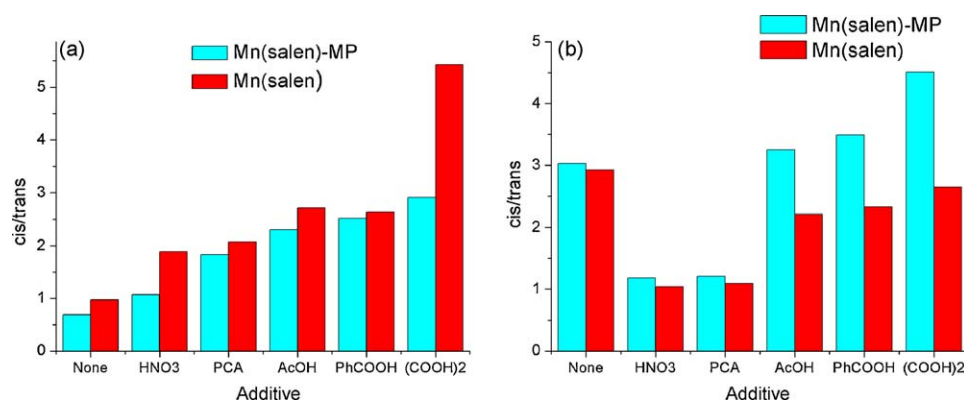

Fig. 2. Stereoselectivity parameters *cis/trans* in the oxidation of *cis*- (a) and *trans*- (b) isomers of 1,2-dimethylcyclohexane by *t*-BuOOH, catalyzed by Mn(salen) (red bars) and Mn(salen)-PM (blue bars) in the presence of various acid additives. Parameter *cis/trans* = [*cis*-ol]/[*trans*-ol], i.e. the ratio of concentrations of the *t*-alcohol (1R,2R or 1S,2S)-1,2-dimethylcyclohexanol and (1R,2S or 1S,2R)-1,2-dimethylcyclohexanol stereoisomers (*cis*-ol and *trans*-ol) formed in the oxidation of *cis*- or *trans*-DMCH. For the reaction conditions, see Table 1. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)
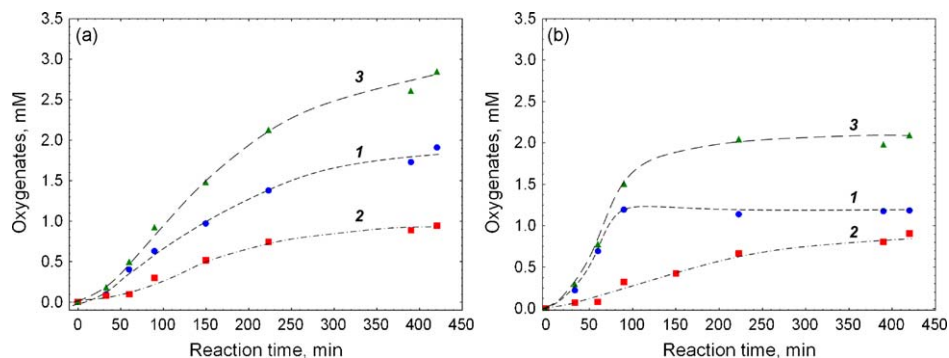
Fig. 3. Accumulation of oxygenates (along the initial 7 h) in the oxidation of *n*-heptane by *t*-BuOOH, catalyzed by Mn(salen)-PM (a) and Mn(salen) (b) in the presence of $(COOH)_2$: (1)—heptanols, (2)—heptanones, (3)—total. Reaction conditions: catalyst (0.16 μmol), $(COOH)_2$ (2.4 mmol), *n*-heptane (2.0 mmol), *t*-BuOOH (5.0 mmol) in CH_3CN (5.0 mL), 50 °C.

the *cis*-isomer of the alcohol. It is known that the *cis*-disubstituted alkenes are more stereoselective substrates than their *trans*-analogues [77,78]. Changes of the *cis/trans* ratios can be induced by varying the catalyst, solvent or additive. For example, chiral quaternary ammonium salts induce a dramatic reversal in epoxidation stereoselectivity (i.e., giving *trans*-epoxide from a *cis*-olefin) [78].

The stereoselectivity of *cis*-DMCH oxidation is lower in the case of the immobilized complex than when using a homogeneous catalyst, but the opposite behaviour is observed in the oxidation of *trans*-DMCH, what is possibly explained by different steric restrictions created by the microenvironment of the polymeric membrane. The obtained results are in line with an earlier study, where grafting of Mn(salen) complexes on polystyrene resin led to an epoxidation activity comparable with that of the respective homogeneous catalysts, but with significantly inversed *cis/trans* ratios of the formed epoxides, due to the steric effects created by the support containing a rigid ligand coordinated to the metal [79].

The oxidation of *n*-octane and *n*-heptane by *t*-BuOOH in the presence of the Mn(salen)-PM and Mn(salen) catalysts leads to a mixture of isomeric alcohols and ketones oxygenated at positions 2, 3 and 4 of the hydrocarbon chain, with turnover numbers (TONs) up to 110 and yields of ca. 1%. No products of alkane oxygenation of terminal CH_3 groups were detected under our reaction conditions. Ketones are usually the main products of the reaction, being formed with selectivities of ca. 80% after 24 h of reaction time (Table 2). No difference in the products composition of the final reaction mixtures was observed before and after treatment with PPh₃ (following the method developed by Shul'pin [65,66]), thus testifying that no alkylhydroperoxides were presented in solution after 24 h. In order to clarify the possible formation of intermediate

alkylhydroperoxides we have monitored the reaction kinetics during the first hours.

The kinetic curves (accumulation of the oxygenates in the reaction of *n*-heptane oxidation) in the presence of Mn(salen)-PM (Fig. 3a) and Mn(salen) (Fig. 3b) are similar. During the first hours, alcohols (heptanol-2, -3 and -4) are the main products, and their concentration grows after treatment of the reaction mixture with PPh₃, thus indicating that alkyl hydroperoxides could be involved as intermediates. Accumulation of ketones (heptanone-2, -3, and -4) is observed since the beginning of the reaction, but their formation proceeds slower than that of the alcohols; the latter thus could be further oxidized by *t*-BuOOH to afford the corresponding ketones.

Fig. 4 shows the regioselectivity parameter C(2):C(3):C(4) concerning the reactivities of H atoms at positions 2, 3 and 4 of the hydrocarbon chain, which has been normalized by taking into account the number of hydrogen atoms at each position (the reactivity of the methylene H atoms at position 3 is chosen to be equal to the unity for both the alcohol and the ketone products). As it can be seen from this figure, the hydrogens at position 2 are more reactive than H atoms at positions 3 and 4 in the presence of Mn(salen)-PM. In contrast, under homogeneous conditions of Mn(salen), the reactivity of the methylene group in the position 4 is higher than those in the positions 2 and 3 (Table 2, entries 1–4).

A similar reactivity (with preferable formation of oxygenated products at the position 4 of the hydrocarbon chain) has been observed in the presence of a dinuclear manganese complex bearing 1,4,7-trimethyl-1,4,7-triazacyclononane in the reaction of *n*-heptane oxidation [76]. In that study, it has been assumed that the long linear hydrocarbon chains exist in aqueous solution in the folded ("hair-pin") conformation. Hence, the position 4 of *n*-

Table 2

Regioselectivity parameter C(2):C(3):C(4) in the oxidation of linear alkanes with *t*-BuOOH catalyzed by Mn(salen)-PM and Mn(salen)[a,b].

Entry	Catalyst	Substrate	Alcohol C(2):C(3):C(4)	Ketone C(2):C(3):C(4)	Ketone selectivity (%)[c]
1	Mn(salen)-PM	*n*-Octane	1.7:1.0:1.1	1.4:1.0:1.0	83
2	Mn(salen)	*n*-Octane	1.0:1.0:1.3	0.9:1.0:1.4	83
3	Mn(salen)-PM	*n*-Heptane	1.3:1.0:1.2	1.6:1.0:1.1	85
4	Mn(salen)	*n*-Heptane	1.0:1.0:1.3	1.0:1.0:1.2	81
5	Mn(salen)-PM	*n*-Hexane	1.0:1.9	1.0:1.2	80
6	Mn(salen)	*n*-Hexane	1.0:1.2	1.0:1.2	80
7	Mn(salen)-PM	*n*-Pentane	1.0:1.3	1.0:1.2	83
8	Mn(salen)	*n*-Pentane	1.0:1.2	1.0:1.2	82

[a] *Reaction conditions*: Catalyst (0.08 μmol), substrate (2.0 mmol), oxidant *t*-BuOOH (5.0 mmol) in acetonitrile (3.0 mL), 24 h, r.t.

[b] C(2):C(3):C(4) = molar ratios of normalized oxygenates at the indicated C-atom positions (the values at positions 3 (C3) or 2 (C2) were fixed as unity in the case of *n*-octane and *n*-heptane or *n*-hexane and *n*-pentane, respectively).

[c] Selectivity (%) towards ketone formation is equal to the molar amount of ketone/total molar amount of products (alcohol and ketone) × 100.
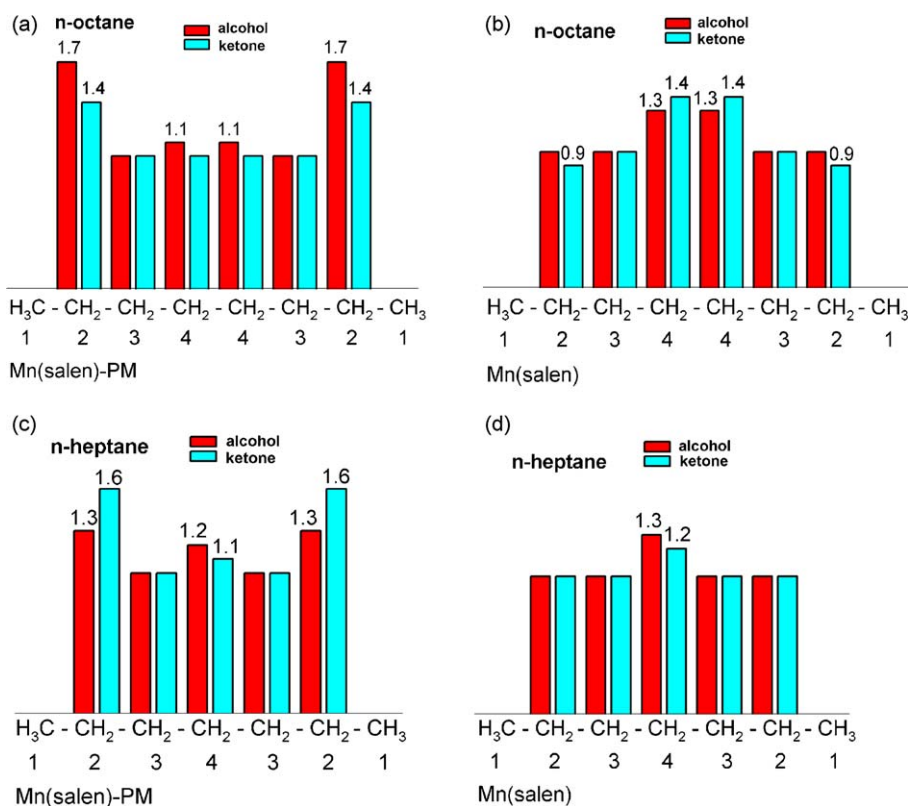
Fig. 4. Reactivity of hydrogen atoms (normalized taking into account the number of H atoms at each position of the hydrocarbon chain, and referenced to C(3) = 1 for both the alcohol and ketone products) in the oxidation of *n*-octane (a and b) and *n*-heptane (c and d) by *t*-BuOOH in the presence of Mn(salen)-PM (a and c) and Mn(salen) (b and d). For reaction conditions, see Table 2.

heptane could be more accessible for hydroxyl radical attack rather than the other positions.

Regioselective oxidations of linear alkanes in aqueous H_2O_2 were achieved using microporous titanosilicalite TS-1 [80,81]. As in our case, only oxidations of methylene groups were observed with TS-1, while the inert methyl groups remained unreacted. However, in contrast to our systems with *n*-heptane and *n*-hexane, it was reported [80] that reactivity of the CH_2 groups at position 3 is ca. 2–3 times higher than those of the other methylene groups. It was then proposed [80] that such an unusual selectivity was due to the narrow hydrophobic cavities of TS-1 in which the oxidation takes place.

In the case of the oxidation of shorter alkane chains (*n*-hexane and *n*-pentane), the reactivity of hydrogen atoms at the position 3 (C3) is higher than that at the position 2 (C2), the latter being fixed as unity (Fig. 5, Table 2, entries 5–8). No products of alkane oxygenation at terminal CH_3 groups are detected.

We have also performed sorption measurements of the alkanes (those used as substrates in the oxidation reactions) by the Mn(salen) containing membranes (Fig. 6). The C_5–C_8 alkanes have a similar polarity and differ only by the size of the hydrocarbon chain. Thus, the shorter chain hydrocarbons, *n*-pentane and *n*-hexane, lead to higher sorption values than *n*-heptane and *n*-octane. This shows the greater difficulties for C_7 and C_8 alkanes to enter into the membrane and could determine the difference in reactivities of hydrogen atoms in the oxidation of the above substrates when using the encapsulated catalyst Mn(salen)-PM.

The different regioselectivities when using supported or homogeneous Mn(salen) catalysts, or varying the length of the hydrocarbon chain, can tentatively be explained by the following considerations. In the case of the supported catalyst, the substrate and the oxidant are allowed to diffuse through the membrane to the catalytic sites where the reaction is taking place. Thus, for the

longer alkanes, the hydrogens at the position 2 (close to the extremity of chain) could be more accessible (due to the presence of the bulk hydrophobic PDMS chains) to the active catalytic centres than those in the middle of the hydrocarbon chain. However, for the shorter alkanes, with a lower steric hindrance, position 2 would not be favoured relatively to 3 which becomes more reactive.

In order to evaluate the possible recycling of the Mn-containing membrane, it was thoroughly washed with CH_3CN under vigorous stirring and then reused for a new set of *n*-heptane oxidation experiments. Unfortunately, the catalytic activity of the recycled membrane was much lower than that of the fresh one, most likely due to the blockage of the active sites, upon adsorption of the reagents on the membrane surface, which were not completely removed during the membrane washing procedure. The activation of the TEOS/PDMS-based membranes is typically a complicated procedure. To avoid the Mn leaching, the membrane washing requires the use of a polar solvent, but such a solvent cannot enter into the membrane, thus making the washing insufficient.

3.2. Toluene oxidation

Oxidations of alkylbenzenes are important transformations in chemical synthesis [82] which, however, normally undergo with a low selectivity, with the formation of various by-products. In particular, the oxidation of toluene usually leads to the formation of benzaldehyde, benzyl alcohol, cresols, benzoic acid and dibenzyl. Both oxidations of the methyl group and/or of the aromatic ring may occur depending on the reaction conditions (type of catalyst, additive, oxidant and solvent) [83–85]. Thus, the design of an efficient process for the selective oxidation of alkylbenzenes appears to be an important task. In the present study, we report (Table 3) the oxidation of toluene with the
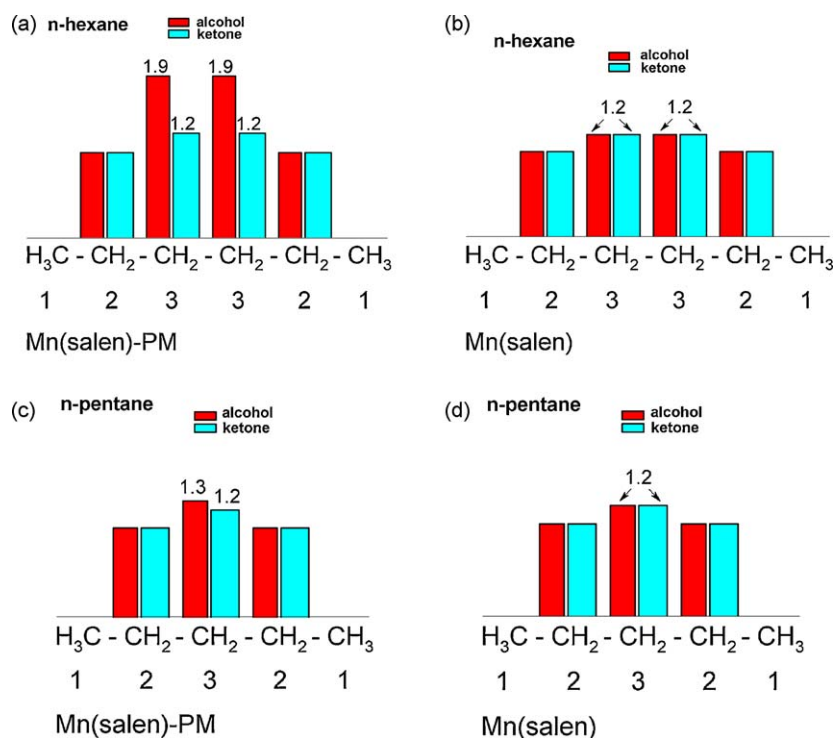
Fig. 5. Reactivity of the hydrogen atoms (normalized taking into account the number of H atoms at each position of the hydrocarbon chain, and referenced to C(2) = 1 for both the alcohol and ketone products) in the oxidation of *n*-hexane (a and b) and *n*-pentane (c and d) by *t*-BuOOH in the presence of Mn(salen)-PM (a and c) and Mn(salen) (b and d).

formation of benzaldehyde as the major product, while benzyl alcohol is generated as a minor one. No oxidations within the aromatic ring were observed.

The performed study on the catalytic transformation of toluene by *t*-BuOOH in the presence of Mn(salen) showed that the system with the catalyst immobilized on the polymeric membrane (total benzaldehyde and benzyl alcohol yield up to 5%, TON up to 1.3×10^3) exhibits a slightly lower activity in comparison with the unsupported catalyst (overall benzaldehyde and benzyl alcohol yield up to 6.6%, TON up to 1.7×10^3). This can be due to natural limitations of heterogeneous catalytic systems, such as the slow diffusion of the reactants to the catalytic site. However, Mn(salen)-PM also displays a rather high catalytic efficiency in terms of TON and leads to a higher selectivity towards benzaldehyde formation (up to 98%) than the unsupported catalyst (up to 92%).

Fig. 6. Sorption (mmol alkane per gram of polymeric membrane) of *n*-alkanes by Mn(salen)-PM.

In the absence of any acid additive, the oxidation proceeds with yields not higher than 1%. The addition of an acid promoter leads to much higher activity and selectivity for both Mn(salen) and Mn(salen)-PM, that achieve the optimum values for ca. 4.8 μmol of acid (i.e., acid-to-catalyst molar ratio of 60, Table 3, entries 1–18). Further increase of the acid additive amount (above 4.8 μmol) does not result in a higher activity in the case of Mn(salen) and even lowers the performance of Mn(salen)-PM (entries 4 and 11, Table 3), probably due to the competition between toluene and additive for the sorption by the membrane. All tested acids exhibit a comparable promoting effect as can be seen from Table 3. Furthermore, the benzaldehyde formation is favoured over that of benzyl alcohol, in the presence of acid additives.

3.3. Mechanistic consideration

The simplified pathway of Scheme 1 can be proposed for the oxidation of alkanes and toluene (RH, with R = alkyl and benzyl, respectively) by *t*-BuOOH catalyzed by Mn(salen) in the presence of an acid additive. Comparison of the selectivity parameters we have obtained in the oxidation of alkanes by *t*-BuOOH in the presence of Mn(salen) with those of other oxidizing systems [1–3,47,50,65,66,69–74,86,87] allows us to conclude that they are different from those found when involving the hydroxyl radical, but close to those when *tert*-butoxyl radical *t*-BuO• is generated [69]. *t*-BuO• is formed upon reduction of *t*-BuOOH by the Mn^{III}(salen) catalyst, generating also a hydroxo-Mn^{IV} derivative (Scheme 1, reaction (1)). This species can further react with *t*-BuOOH, forming Mn^{IV}(salen)(OOBu-t) (reaction (2)), which can decompose to yield the *tert*-butylperoxyl radical *t*-BuOO• (reaction (3)). This can dismutate leading to *t*-BuO• and dioxygen (reaction (4)) [69,88–90].

The *tert*-butoxyl radical (generated in reactions (1) and (4)) abstracts an H-atom from the hydrocarbon with the formation of alkyl (in the case of alkane) or benzyl (in the case of toluene oxidation) radicals R• (reaction (5)). The process can then proceed
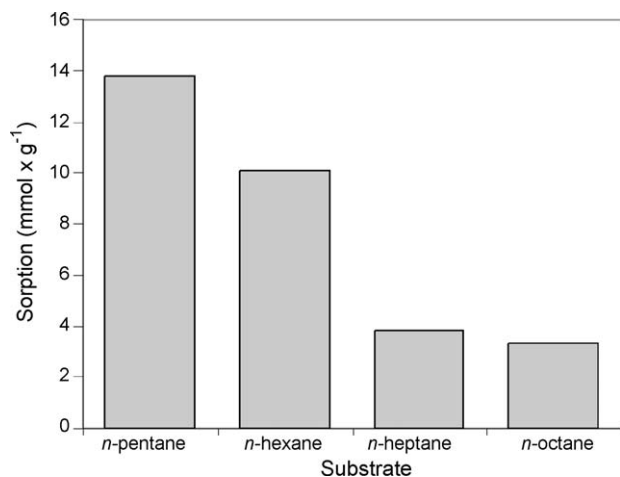
Table 3
Oxidation of toluene with t-BuOOH catalyzed by Mn(salen)-PM and Mn(salen)[a].

Entry	Catalyst	Additive	Additive amount (μmol)	Total yield[b] (%)	TON[c]	Product distribution (%)	
						Benzaldehyde	Benzyl alcohol
1	Mn(salen)-PM	None	–	0.3	82	86	14
2		HNO_3	2.4	1.3	320	92	8
3		HNO_3	4.8	4.1	1020	97	3
4		HNO_3	7.2	3.3	830	95	5
5		PhCOOH	2.4	1.2	300	85	15
6		PhCOOH	4.8	3.8	940	93	7
7		PCA	2.4	1.4	350	89	11
8		PCA	4.8	3.9	960	95	5
9		$(COOH)_2$	2.4	2.3	580	91	9
10		$(COOH)_2$	4.8	5.1	1290	98	2
11		$(COOH)_2$	7.2	4.2	1060	96	4
12	Mn(salen)	None	–	1.1	270	87	13
13		HNO_3	4.8	6.2	1560	87	13
14		HNO_3	7.2	6.3	1560	92	8
15		PhCOOH	4.8	5.7	1420	89	11
16		PCA	4.8	6.0	1490	87	13
17		$(COOH)_2$	4.8	6.6	1660	90	10
18		$(COOH)_2$	7.2	6.6	1650	87	13

[a] *Reaction conditions*: Catalyst (0.08 μmol), toluene (2.0 mmol), t-BuOOH (5.0 mmol) in acetonitrile (3.0 mL), r.t., 24 h.
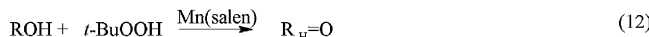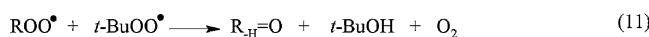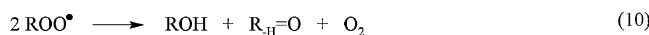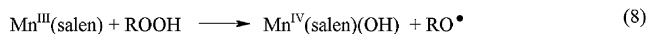[b] Benzaldehyde + benzyl alcohol, based on toluene.
[c] TON was estimated as moles of products (benzaldehyde and benzyl alcohol)/mol of catalyst.

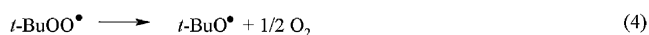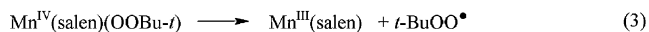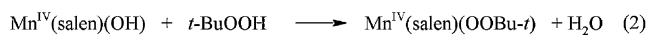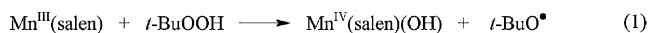via formation of the organo-peroxyl radical ROO• (upon reaction of R• with O_2) and the organo-hydroperoxide ROOH (reactions (6) and (7)) which could also undergo homolytic decomposition to the organooxyl RO• radical (reaction (8)). RO• would form the alcohol ROH and R• by H-abstraction from the substrate (reaction (9)), whereas ROO• would either decompose (reaction (10)) to the alcohol and the ketone, or aldehyde (in the case of toluene), or regenerate ROOH and R• on H-abstraction from the hydrocarbon (reaction (7)), as has been proposed for some metal-catalyzed alkane oxidations by O_2 [1–3,59,65,66]. The organo-peroxyl radical ROO• can also undergo the mixed bimolecular Russell termination to form ketone (or aldehyde) and t-BuOH (reaction (11)), increasing the ketone (or aldehyde) selectivity [91].

In addition, the ketone can be generated from the Mn(salen)-assisted further oxidation of the alcohol (reaction (12)). Besides, blank experiments using alcohol as a substrate in the same conditions showed that ketone can be obtained in high yields (reaction (12)).

Such a type of mechanism is similar to that proposed for the Co(salen)-catalyzed oxidation of phenols and anilines with t-BuOOH [88–90].

$$Mn^{III}(salen) + t\text{-BuOOH} \longrightarrow Mn^{IV}(salen)(OH) + t\text{-BuO}^{\bullet} \quad (1)$$

$$Mn^{IV}(salen)(OH) + t\text{-BuOOH} \longrightarrow Mn^{IV}(salen)(OOBu\text{-}t) + H_2O \quad (2)$$

$$Mn^{IV}(salen)(OOBu\text{-}t) \longrightarrow Mn^{III}(salen) + t\text{-BuOO}^{\bullet} \quad (3)$$

$$t\text{-BuOO}^{\bullet} \longrightarrow t\text{-BuO}^{\bullet} + 1/2\,O_2 \quad (4)$$

$$t\text{-BuO}^{\bullet} + RH \longrightarrow R^{\bullet} + t\text{-BuOH} \quad (5)$$

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \quad (6)$$

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \quad (7)$$

$$Mn^{III}(salen) + ROOH \longrightarrow Mn^{IV}(salen)(OH) + RO^{\bullet} \quad (8)$$

$$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet} \quad (9)$$

$$2\,ROO^{\bullet} \longrightarrow ROH + R_{\text{-H}}{=}O + O_2 \quad (10)$$

$$ROO^{\bullet} + t\text{-BuOO}^{\bullet} \longrightarrow R_{\text{-H}}{=}O + t\text{-BuOH} + O_2 \quad (11)$$

$$ROH + t\text{-BuOOH} \xrightarrow{\text{Mn(salen)}} R_{\text{-H}}{=}O \quad (12)$$
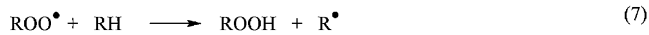
Scheme 1. Simplified pathway for the oxidation of alkanes and toluene (RH, with R = alkyl and benzyl, respectively) by t-BuOOH in the presence of Mn(salen).

However, the promoting role of the acid additive and its influence on the stereo-configuration of the formed products in the oxidation of isomeric 1,2-dimethylcyclohexanes still remain somehow unclear, although we expect that acids can be involved in proton-transfer steps leading to the activation of the Mn(salen) species and to unsaturation of the metal centre via protonation of the ligand, as well as enhancement of the oxidizing properties of the metal catalyst, facilitating O–O bond cleavage of t-BuOOH due to the presence of a high proton concentration, and hampering the decomposition of the oxidant [41,42,46,92].

4. Conclusions

The catalytic properties of a Mn(salen) complex under both heterogeneous (immobilized on PDMS-based membrane) and homogeneous conditions have been evaluated towards the oxidation of various linear and cyclic alkanes in the presence of acid promoters. The selectivity parameters of such oxidations catalyzed by Mn(salen) under homogeneous conditions are found to be different from those achieved with Mn(salen)-PM. The stereoselectivity also depends on the type of the acid promoter used and the highest values have been achieved in the presence of oxalic acid. The regioselectivity in the presence of Mn(salen)-PM depends on the length of the hydrocarbon chain, being in accord with the hydrocarbon sorption profile. The hydrogens at the position 2 in the higher (C7, C8) alkanes (close to the extremity of the chain) appear to be more accessible in view of the presence of the bulky hydrophobic PDMS chains and thus are preferably oxygenated. In the lower (C5, C6) alkanes, both sorption and diffusion appear to favour the attack at the position 3. No products of alkane oxygenation at the terminal CH_3 groups were detected. This lack of reactivity of the primary carbon is in accord with a radical mechanism. The achieved selectivity parameters are close to those reported earlier [69] for other oxidizing systems that proceed with participation of the *tert*-butoxyl radical. The involvement of the alkyl hydroperoxide (ROOH) as a primary product of alkane oxygenation has been confirmed but, after the prolonged reaction time, the ketone predominates in the reaction mixture and ROOH is no longer detected.

Besides, the selective oxidation of toluene to benzaldehyde as the main product has been achieved by the same systems. This process is also promoted by an acid additive, proceeding with

preferable oxygenation of the methyl group, leading to TONs up to 1.7×10^3. No oxidation of the aromatic ring in toluene has been observed, and the highest selectivity towards benzaldehyde formation is achieved with the supported catalyst.

Acknowledgments

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