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

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Mild oxidations with t-BuOOH of linear (n-pentane, n-hexane, n-heptane and n-octane) and cyclic (1,2-dimethylocyclohexane) 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-butylsalicylideno)-1,2-cyclohexanediimine(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− and alkylperoxy (ROO•) radicals. The tolouene 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 × 103).

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, phthalocyanines, chlorins, Schiff bases and triazacyclononanes have been extensively studied as alkane oxidation catalysts [19–27]. However, there are relatively few reports on alkane oxidations catalyzed by Mn(salen) complexes [salen = (R,R)-N,N-bis(3,5-di-tert-butylsalicylideno)-1,2-cyclohexanediimine(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-

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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], metallophthalocyanines [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. H₂O₂ is less efficient since the hydrophobic membrane creates a barrier against H₂O₂, 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-butylsalicyldienato)-1,2-cyclohexanedi-amine(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 pentaerythritoltriacylate (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 CH₃CN (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 as 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 (PPh₃) 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 CH₂Cl₂), 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.
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)*.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additive</th>
<th>cis/trans&lt;sup&gt;b&lt;/sup&gt; cis-DMCH</th>
<th>trans-DMCH</th>
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<tr>
<td>1</td>
<td>Mn(salen)-PM</td>
<td>None</td>
<td>0.69</td>
<td>3.03</td>
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<td>2</td>
<td>Mn(salen)</td>
<td>None</td>
<td>0.97</td>
<td>2.92</td>
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<tr>
<td>3</td>
<td>Mn(salen)-PM</td>
<td>HNO₃</td>
<td>1.07</td>
<td>1.18</td>
</tr>
<tr>
<td>4</td>
<td>Mn(salen)</td>
<td>HNO₃</td>
<td>1.89</td>
<td>1.04</td>
</tr>
<tr>
<td>5</td>
<td>Mn(salen)-PM</td>
<td>PCA</td>
<td>1.83</td>
<td>1.21</td>
</tr>
<tr>
<td>6</td>
<td>Mn(salen)</td>
<td>PCA</td>
<td>2.07</td>
<td>1.09</td>
</tr>
<tr>
<td>7</td>
<td>Mn(salen)-PM</td>
<td>AcOH</td>
<td>2.30</td>
<td>3.25</td>
</tr>
<tr>
<td>8</td>
<td>Mn(salen)</td>
<td>AcOH</td>
<td>2.71</td>
<td>2.21</td>
</tr>
<tr>
<td>9</td>
<td>Mn(salen)-PM</td>
<td>PhCOOH</td>
<td>2.52</td>
<td>3.49</td>
</tr>
<tr>
<td>10</td>
<td>Mn(salen)</td>
<td>PhCOOH</td>
<td>2.63</td>
<td>2.33</td>
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<td>11</td>
<td>Mn(salen)-PM</td>
<td>(COOH)₃₂</td>
<td>2.91</td>
<td>4.51</td>
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<tr>
<td>12</td>
<td>Mn(salen)</td>
<td>(COOH)₃₂</td>
<td>5.43</td>
<td>2.65</td>
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</table>

<sup>a</sup> 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.

<sup>b</sup> Parameter cis/trans = [cis-al] /[trans-al], 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 weighed again. The sorption of alkanes on the membrane was obtained by determining their swelling using the following expression [67].

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

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 stereochromical configuration is characteristic of a concerted reaction mechanism (in enzymes, however, the retention can be imposed by the active site geometry), loss of the stereochromical 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 stereochromical 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 H₂O₂ [76].

The oxidation of trans-1,2-dimethylcyclohexane is also not stereoselective in the presence of HNO₃ 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...
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 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 CH₃ groups were detected under our reaction conditions. Ketones are usually the main products of the reaction, being more stereoselective substrates than their alkene analogues [77,78]. Changes of the 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].

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-

![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 CH₃CN (5.0 mL), 50°C.](image1)

Table 2

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn(salen)-PM</td>
<td>n-Octane</td>
<td>1.7:1.0:1.1</td>
<td>1.4:1.0:1.0</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>Mn(salen)</td>
<td>n-Octane</td>
<td>1.0:1.0:1.3</td>
<td>0.9:1.0:1.4</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>Mn(salen)-PM</td>
<td>n-Heptane</td>
<td>1.3:1.0:1.2</td>
<td>1.6:1.0:1.1</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>Mn(salen)</td>
<td>n-Heptane</td>
<td>1.0:1.0:1.3</td>
<td>1.0:1.0:1.2</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>Mn(salen)-PM</td>
<td>n-Hexane</td>
<td>1.0:1.9</td>
<td>1.0:1.2</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>Mn(salen)</td>
<td>n-Hexane</td>
<td>1.0:1.2</td>
<td>1.0:1.2</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>Mn(salen)-PM</td>
<td>n-Pentane</td>
<td>1.0:1.3</td>
<td>1.0:1.2</td>
<td>83</td>
</tr>
<tr>
<td>8</td>
<td>Mn(salen)</td>
<td>n-Pentane</td>
<td>1.0:1.2</td>
<td>1.0:1.2</td>
<td>82</td>
</tr>
</tbody>
</table>

* 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.

* 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).

* Selectivity (%) towards ketone formation is equal to the molar amount of ketone/total molar amount of products (alcohol and ketone) × 100.
heptane could be more accessible for hydroxyl radical attack rather than the other positions.

Regioselective oxidations of linear alkanes in aqueous H$_2$O$_2$ 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 C5–C8 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 C7 and C8 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$_3$CN 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
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 $1.3 \times 10^3$) exhibits a slightly lower activity in comparison with the unsupported catalyst (overall benzaldehyde and benzyl alcohol yield up to 6.6%, TON up to $1.7 \times 10^3$). 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%).

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 MnIII(salen) catalyst, generating also a hydroxo-MnIV derivative (Scheme 1, reaction (1)). This species can further react with t-BuOOH, forming MnIV(salen)(OOBu-t) (reaction (2)), which can decompose to yield the tert-butyperoxy 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...
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 organooxy \(R^{•}\) (reaction (8)). ROO\(^{•}\) would form the alcohol ROH and \(R^{•}\) whereas ROO\(^{•}\) regenerates ROOH and \(R^{•}\) alcohol and the ketone, or aldehyde (in the case of toluene), or alkane oxidations by O\(_2\) [1–3,59,65,66]. The organo-peroxyl radical (reaction (7)), as has been proposed for some metal-catalyzed oxidations of toluene with \(t\)-BuOOH [88–90].

**Scheme 1.** Simplified pathway for the oxidation of alkanes and toluene (RH, with \(R = \text{alkyl and benzyl, respectively}\)) 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 have been confirmed but, after the prolonged reaction time, the ketone predominates in the reaction product of alkane oxygenation at the terminal CH\(_3\) groups were detected. 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-butylxyl 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 benzoaldehyde as the main product has been achieved by the same systems. This process is also promoted by an acid additive, proceeding with

### Table 3

Oxidation of toluene with \(t\)-BuOOH catalyzed by Mn(salen)-PM and Mn(salen)\(^{•}\).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additive</th>
<th>Additive amount ((\mu)mol)</th>
<th>Total yield(^{b}) (%)</th>
<th>TON(^{c})</th>
<th>Product distribution (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>Mn(salen)-PM</td>
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<td>–</td>
<td>0.3</td>
<td>82</td>
<td>86</td>
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<tr>
<td>2</td>
<td>Mn(salen)-PM</td>
<td>HNO(_3)</td>
<td>2.4</td>
<td>1.3</td>
<td>320</td>
<td>92</td>
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<td>3</td>
<td>Mn(salen)-PM</td>
<td>HNO(_3)</td>
<td>4.8</td>
<td>4.1</td>
<td>1020</td>
<td>97</td>
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<tr>
<td>4</td>
<td>Mn(salen)-PM</td>
<td>HNO(_3)</td>
<td>7.2</td>
<td>3.3</td>
<td>830</td>
<td>95</td>
</tr>
<tr>
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<td>Mn(salen)-PM</td>
<td>PhCOOH</td>
<td>2.4</td>
<td>1.2</td>
<td>300</td>
<td>85</td>
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<tr>
<td>6</td>
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<td>3.8</td>
<td>940</td>
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<td>1.4</td>
<td>350</td>
<td>89</td>
</tr>
<tr>
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<td>4.8</td>
<td>3.9</td>
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<td>95</td>
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<tr>
<td>9</td>
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<td>2.3</td>
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<td>91</td>
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<td>1290</td>
<td>98</td>
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<td>4.2</td>
<td>1060</td>
<td>96</td>
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<td>6.2</td>
<td>1560</td>
<td>87</td>
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<td>6.3</td>
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<td>7.2</td>
<td>6.6</td>
<td>1650</td>
<td>87</td>
</tr>
</tbody>
</table>

\(^{a}\) Reaction conditions: Catalyst (0.08 mol), 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.
preferable oxygenation of the methyl group, leading to TONS up to 1.7 × 10^5. 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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References