Epoxidation of olefins catalyzed by novel Mn(III) and Mo(IV)-Salen complexes immobilized on mesoporous silica gel
Part II: Study of the catalytic epoxidation of olefins

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Abstract

Mn(III) and Mo(IV)-Salen complexes homogeneous and immobilized on a silica surface have been tested in the catalytic epoxidation of cyclooctene and cyclohexene with *tert*-butylhydroperoxide (TBHP) and hydrogen peroxide (HP) as an oxidant. The effects of reaction conditions on the epoxide yield as well as the epoxidation rate with different catalysts have been established. The catalytic decomposition of TBHP by manganese and molybdenum-Salen complexes has been studied. The peptide immobilized Salen complexes were compared in catalytic activity with ester bound ones. The immobilized catalysts show stable catalytic activity in manifold reuses. The Mo-Salen complexes homogeneous as well as immobilized exhibited high catalytic activity for the epoxidation of cyclooctene, whereas Mn-Salen complex systems cause additionally non-productive decomposition of hydroperoxide.

1. Introduction

Partial oxidation of alkenes to epoxides and reaction products based on epoxides are both of academic and industrial interest. Various epoxides are among the most widely used intermediates in organic synthesis, pharmaceuticals as well as polymer production, acting as precursors for complex molecules due to the strained oxirane ring [1]. They react to provide industrially important products such as surfactants, detergents, antistatic agents and corrosion protection agents, lubricating oils, textiles and cosmetics [2]. Besides the epoxidation is an important step in the syntheses of various biologically active compounds. In particular, cyclooctene and cyclohexene oxides are valuable organic intermediates used in the synthesis of products such as chiral pharmaceuticals, pesticides, epoxy paints, rubber promoters and dyestuffs.

In order to make the epoxidation process cleaner, safer and more efficient, the use of catalysts is mandatory. As a result of the apparent interest in the improvement of epoxide synthesis many investigations have been undertaken to develop catalysts for epoxidation, e.g. supported metal oxides [3,4] as well as homogeneous transition metal complexes [5]. Metal complexes of the Schiff base with a N_2O_2 coordination sphere, which are known as Salen complexes (Salen—N,N'-bis(salicylidene)-ethylendiamine), have been reported by Kochi and co-workers [6] and later on by Jacobsen and co-workers [7], Katsuki and co-workers [8] as one of the most efficient homogeneous catalysts in asymmetric catalytic reactions. Their applications have grown rapidly and a broad range of asymmetric catalytic reactions has been described including oxidations, additions and reductions such as epoxidation of olefins, epoxide ring opening, Diels-Alder reaction, imine cyanation, conjugate addition,

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carbon dioxide insertion into epoxides, etc. [5,9–12]. Various metal-Salen complexes in the homogeneous phase such as manganese(III) [6], chromium(III) [13] and nickel(II) [14] Salen have been used for the epoxidation of olefins.

The heterogenization of metal-Salen systems by immobilizing the complex on an insoluble polymer support [15], porous materials such as zeolites, MCM-41 and analogous materials [16–19] or intercalation in clays [20,21] has recently received significant attention. This improvement permits to turn to the advantages of both homogeneous (enantioselectivity, activity) and heterogeneous (separation, recovery, recycling) catalysts. Therefore, the immobilization of homogeneous catalysts allows to overcome the problems with separation and reuse and, thus, greatly amends the properties of the catalysts and their commercial value.

We recently reported the syntheses of new active and stable immobilized Mn(III) and Mo(IV)-Salen complexes on organo-modified silica supports and their characterization by spectroscopic methods. In this first part we presented two novel methods for the covalent attachment of manganese and molybdenum-Salen complexes [22].

In this paper, we report the results of the study on the catalytic activity in the epoxidation reaction with the homogeneous and the immobilized Salen complexes.

2. Experimental

2.1. Catalyst

The homogeneous Mn(III) and Mo(IV)-Salen complexes as well as the complexes covalently immobilized on organo-modified silica surface by peptide and ester bonding (Scheme 1) were used for the catalytic epoxidation of olefins [22,23]. Both the unsupported metal-Salen complexes and the immobilized complexes used for the catalytic experiments were preliminary dried at 80 °C and 80 mbar to remove adsorbed water and residuals of organic compounds.

2.2. Catalytic tests

The homogeneous (**1**, **2**) and immobilized (**3**, **4**) manganese and molybdenum-Salen complexes (Scheme 1) were explored in the catalytic epoxidation of cyclooctene and cyclohexene with *tert*-butylhydroperoxide (TBHP) and hydrogen peroxide (HP) as oxidants. Catalytic experiments were performed in a 10 ml pear-shaped two-necked flask supplied with a magnetic stirrer and backflow condenser. The flask was thermostat-controlled where the temperature was maintained constant to within ±1 °C. The side neck of the flask equipped with a septum was used for

1a, 2a   **1b, 2b**

3a, 4a   **3b, 4b**
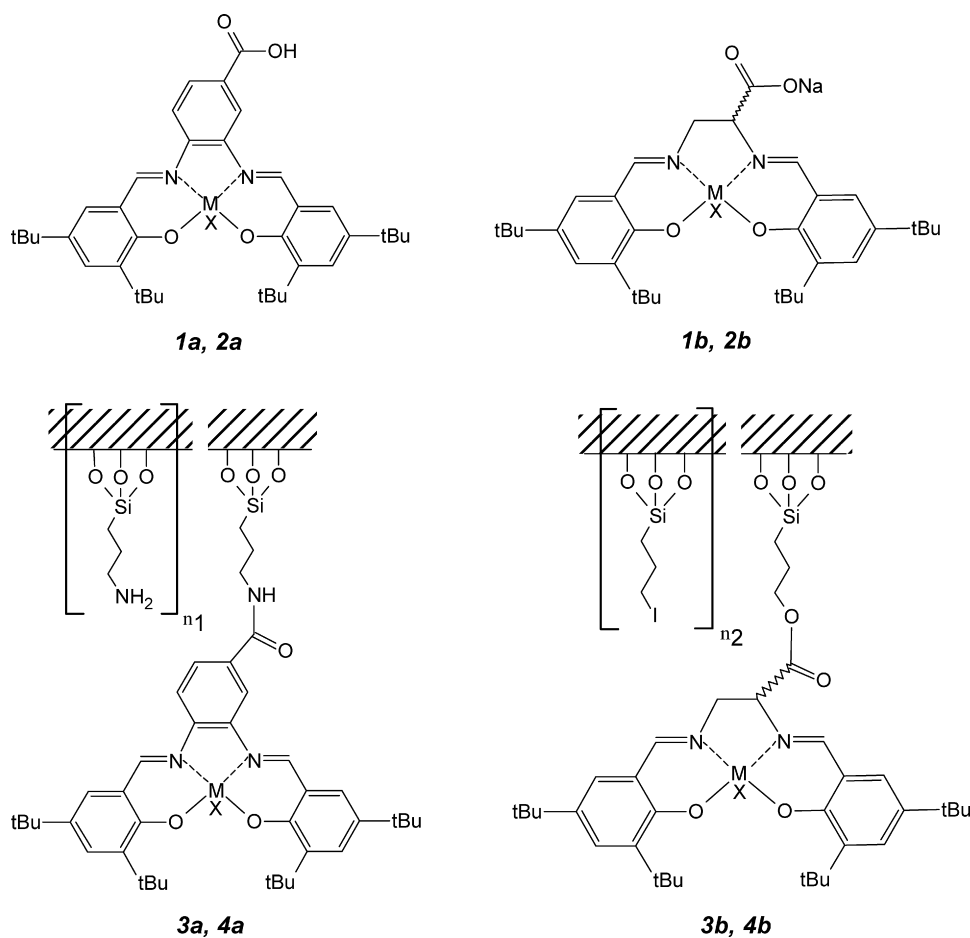
Scheme 1. Homogeneous and immobilized metal-Salen complexes used as catalysts in the epoxidation of olefins (**1**, **3**: MX = Mn(III)–Cl; **2**, **4**: MX = Mo(IV)=O; **a**: precursor for peptide immobilization, peptide bound immobilized Salen complex; **b**: precursor for ester immobilization, ester bound immobilized Salen complex; n_1: 7–9; n_2: 17–100).

sampling of the reaction mixture during the catalytic process for analysis. Unless otherwise stated, the typical reaction mixture for catalytic and kinetic studying was composed of 1.7 mmol of olefin, 5.1 mmol of the hydroperoxide, 0.015 mmol of catalyst (in case of the immobilized complex the amount was calculated via the active centers of metal), 0.1 ml of chlorobenzene as an internal standard and 1.5 ml of toluene as solvent. The yield of epoxide (%) was calculated according to the initial amount of olefin. The conversion of hydroperoxide and olefin (%) was calculated on basis of the amount of starting materials, i.e. hydroperoxide and olefin, respectively.

2.3. Chemicals

The solvents used for the catalytic reactions were purchased as extra dry from Acros Organics and used without further purification. The olefins, hydroperoxides, gas chromatographical standards and epoxides as well as all additional chemicals were used as received. *tert*-Butylhydroperoxide (6.0 M solution in *n*-nonane) was purchased from Aldrich.

2.4. Analyses

GS: Gas chromatography was used for the identification and the quantification of the reaction products. All analyses were performed with a gas chromatograph (Chrompack CP-9000) equipped with a DB-5 capillary column (length: 30 m, internal diameter: 320 μm, film thickness: 0.5 μm) and a flame ionization detector. The following temperature program was installed: $T = 45$–$220\,^\circ$C with a heating rate of 15 K min^{-1}, initial hold time is 8 min. Chlorobenzene and *n*-nonane were used as internal standards. The injector temperature was $220\,^\circ$C allowing to analyze TBHP using the mentioned type of column. Some experiments using iodometric titration method were carried out to determine additionally to GC analysis the hydroperoxide content.

ICP-OES: The metal-Salen complex loading in immobilized catalysts was confirmed and the amount of metal-Salen complex that was leached from the immobilized catalyst into the reaction mixture during catalytic epoxidation was defined by elemental analysis of the metal using inductively coupled plasma-optical emission spectrometry (Varian Vista ICP-OES in Wolfener Analytik GmbH of Bitterfeld, Germany). The detection limit for metal content on the supported matrixes of this method is ca. 0.01 wt.%, with an accuracy of about ±5 to ±20% at lower concentrations. To confirm the absence of metal leached to the solution after reaction an additional more sensitive qualitative analysis was performed (the sensitivity is $<2 \times 10^{-4}\%$) [24].

2.5. Reuse of the immobilized catalyst

After the first and all following catalytic runs of the heterogeneous (immobilized) catalysts the recovering procedure of the catalyst was the following: the silica-supported catalysts were washed once with toluene followed by double washing using dichloromethane. The catalyst was then separated from the solvent by decantation and dried under slightly reduced pressure (80 mbar) at $50\,^\circ$C for 1 h.

3. Results and discussion

3.1. Characterization of the immobilized metal-Salen complexes using ICP-OES

The manganese and molybdenum content in the immobilized Mn- and Mo-Salen complexes **3a**, **3b**, **4a** and **4b** was determined using ICP-OES analysis. After some optimization of the synthesis of the heterogeneous catalysts the following results were obtained 1.2 (**3a**) and 1.5 wt.% (**4a**) for the Mn and Mo content, respectively, in case of peptide bound immobilization. Thus, the concentration of the metal-Salen complexes with respect to silica (SiO$_2$) is 0.22 for **3a** and 0.16 mmol g^{-1} for **4a**, respectively (Table 1). For the ester immobilization the results are the following: 0.41 and 0.1 wt.% (0.07 and 0.01 mmol g^{-1}) of manganese (**3b**) and molybdenum (**4b**), respectively.

The results demonstrate that the percentage of peptide interaction of the Salen complex with amino-functionalized silica is ca. 13%, hence, the content of free aminopropyl groups after immobilization with respect to anchored molecules of Salen complex (*n*) is about 7–9 (Scheme 1). The corresponding results for ester immobilized complexes show considerably lower loading of Salen complexes inside the porous silica structure in comparison to the peptide immobilized catalysts: the percentage of ester interaction is ca. 6% for the Mn-Salen complex and ca. 1% for the Mo-Salen complex. Consequently, the number of free iodopropyl groups corresponding to one Mn or Mo-Salen molecule is about 17 or 100, respectively (Table 1). Such differences can be explained by the higher reactivity of the carboxylic group in the Salen complex towards the amino-functionalized silica in comparison to the reactivity of the Salen complex with the sodium salt of the carboxylic acid group towards the iodo-functionalized silica. The metal-Salen complex loading (the content of active species) is of significance for the use as hetero-

Table 1
Metal-Salen complex loading, percentage of immobilization and calculated amount of free amino- and iodopropyl groups for **3a**, **4a**, **3b** and **4b** catalysts

Way of the immobilization	Catalyst	Metal-Salen loading (mmol g^{-1})	Percentage of immobilizing (%)	Relation of free functionalized groups to covered ones
Peptide bound	**3a** (Mn)	0.22	15	7 (aminopropyl)
	4a (Mo)	0.16	11	9 (aminopropyl)
Ester bound	**3b** (Mn)	0.07	6	17 (iodopropyl)
	4b (Mo)	0.01	<1	>100 (iodopropyl)

geneous catalysts. It was comparable or even better than reported for other grafted complexes described earlier [25,26].

3.2. The influence of free amino- and iodopropyl groups on the catalytic activity

Firstly, the possible influence of residual free amino- and iodopropyl groups of the silica surface on the hydroperoxide decomposition was investigated in test experiments. The results showed that for TBHP in toluene at 60 °C the presence of the free amino- and iodopropyl groups, respectively, i.e. suspended organo-modified silica did not cause a decomposition of hydroperoxide. Secondly, to exclude any probability of the influence of the amino- and iodo-functionalized surface groups on the catalytic epoxidation, e.g. epoxide ring opening of the resulting epoxide, experiments with homogeneous Salen complexes mixed with an amount of organo-functionalized silica corresponding to the immobilized case were performed and showed that there was no difference in epoxidation results for such mixtures in comparison to the pure homogeneous catalyst.

3.3. Epoxidation of cyclooctene catalyzed by homogeneous Mn- and Mo-Salen complexes

To compare the catalytic activity of homogeneous and immobilized metal-Salen complexes identical epoxidation reactions of the Mn- and Mo-Salen complexes in homogeneous conditions were carried out. The epoxidation of cyclooctene with Mn-Salen complex **1a** was carried out at 45, 60 and 75 °C. Fig. 1 shows a comparison of cyclooctene oxide formation (open points) with *tert*-butylhydroperoxide decomposition (filled points). The results demonstrate a fast non-productive conversion of TBHP by the Mn-Salen complex. It must be noted that the initial amount of hydroperoxide is three times higher in comparison to olefin. This non-productive conversion of the hydroperoxide is the reason why the epoxidation process is limited to a yield below 50%. An increase in temperature causes additional thermal hydroperoxide decomposition and consequently leads
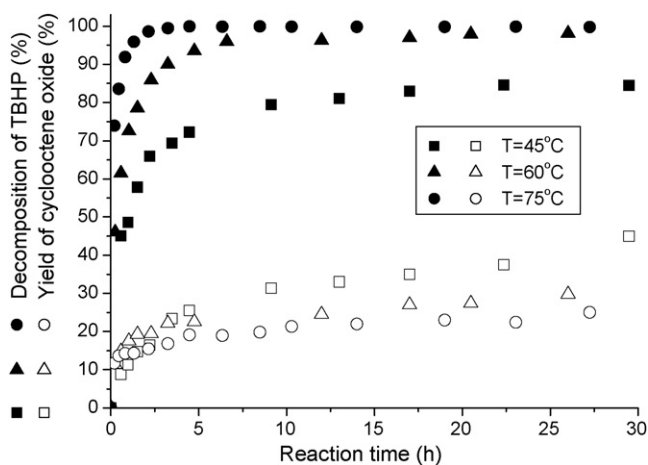

Fig. 1. Temperature effect on the catalytic epoxidation of cyclooctene with the homogeneous Mn-Salen complex **1a**. The reaction mixture was composed as following: cyclooctene/TBHP/catalyst (Mn) = 1/3/0.01.
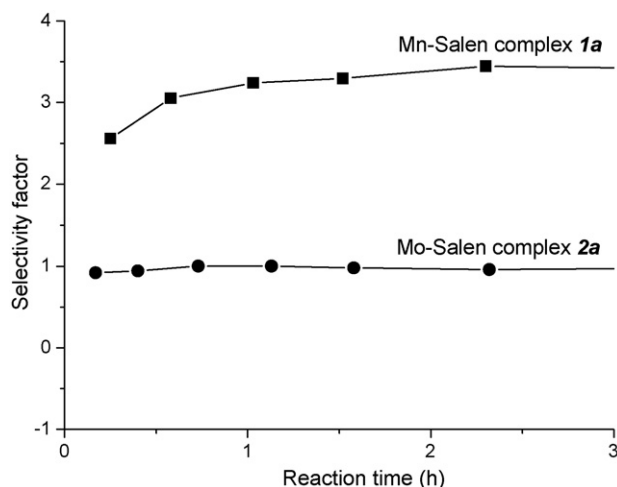

Fig. 2. The selectivity factor SF (Eq. (1)) at 60 °C during cyclooctene epoxidation in presence of the homogeneous manganese **1a** and molybdenum **2a** catalysts.

to even lower selectivity to epoxide formation. TBHP was also decomposed by the Mn-Salen complex **1a** even in absence of the olefin (*T* = 60 °C). After 5 h of reaction the peroxide was 90% converted. In case of cyclooctene epoxidation with the homogeneous Mo-Salen complex **2a** the increase of temperature from 45 to 80 °C led to an increase of epoxide yield while the TBHP conversion also increased but in accordance to the epoxide formation. At 80 °C the epoxide yield amounted to 100% after 20 min of the reaction, in case of 45 °C after 45 min.

To confirm the activity of metal catalysts for the selective formation of epoxide a selectivity factor (SF) was calculated:

$$SF = \frac{\Delta C\,(TBHP)}{\Delta C\,(cyclooctene)}, \tag{1}$$

where $\Delta C\,(TBHP)$ and $\Delta C\,(cyclooctene)$ are mole consumption of TBHP and cyclooctene, respectively.

In Fig. 2 the result for the Mo-Salen complex **2a** shows that the selectivity factor is nearly 1 that means 100% selectivity to the formation of product, whereas the Mn-Salen complex **1a** the selectivity factor is about 3 which confirms that the Mn containing complex apart from the epoxidation of olefin causes the non-productive decomposition of hydroperoxide. Thus, 2/3 part of starting TBHP is decomposed in presence of manganese and only about 1/3 part is consumed for formation of epoxide.

3.4. Comparison of the epoxidation of cyclooctene catalyzed by the homogeneous and by the immobilized catalyst

To confirm that the epoxidation reactions are catalyzed in heterogeneous conditions as well, and that a possible small amount of leaching of the metal-Salen complex does not contribute to the conversion of the olefin, a direct comparison of the yield of formed epoxide between the homogeneous Mn and Mo-Salen complexes as a precursor for anchorage (**1a** and **2a**) and the pep-
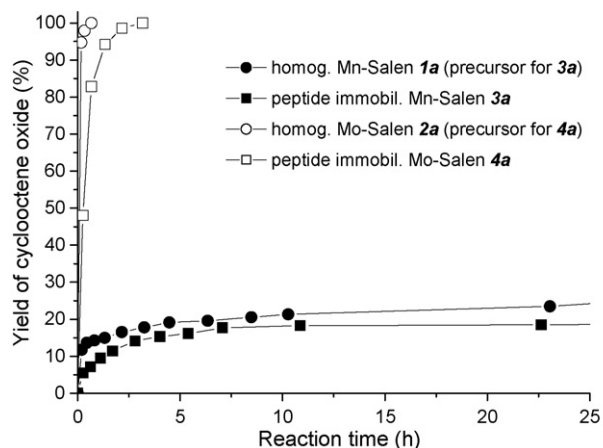
Fig. 3. Comparison of the catalytic activity of the homogeneous (**1a**: Mn and **2a**: Mo) and the peptide immobilized Mn (**3a**) and Mo (**4a**) Salen complexes, respectively, in the epoxidation of cyclooctene at 75 °C with TBHP as oxidant.

tide immobilized Mn and Mo-Salen complex systems (**3a** and **4a**) at the same experimental conditions is shown in Fig. 3. The results demonstrate that there is no large difference in catalytic activity in case of the peptide immobilized metal-Salen complexes in comparison to the homogeneous ones. The observed small decrease in epoxide yield can be explained by a possible diffusion and steric hindrance inside the porous material. Thus, the obtained peptide immobilized Mo-Salen complex showed high activity and selectivity in the epoxidation of cyclooctene towards formation of epoxide. No retarding effect on the epoxidation was observed for Mo-Salen complexes caused by the interaction of the formed *tert*-butanol with metal center in contrast to results reported recently for molybdenum(VI) containing complexes immobilized on MCM-41 in the epoxidation of cyclooctene [25,27]. The deactivation by alcohols is typical for dioxomolybdenum(VI) complexes of the general type $MoO_2X_2L_n$. It was however not found for our Salen systems.

To compare the catalytic activity of heterogenized catalysts prepared by the use of different immobilization procedures experiments with unsupported molybdenum-Salen complexes (**2a** and **2b**) as homogeneous catalysts and peptide (**4a**) and ester (**4b**) bound immobilized Mo-Salen complexes as heterogeneous catalysts were performed in the epoxidation of cyclooctene at identical conditions at 75 °C (Fig. 4). It can be seen that the ester bound immobilized catalyst **4b** is strongly inferior to the peptide immobilized system **4a** in catalytic activity despite the fact that the amount of active metal centers was in both cases identical. The amount of heterogeneous catalyst for the same catalytic reaction in case of peptide immobilization (~0.1 g) differed from the ester immobilized complex (~1.5 g) whereas the other reaction components were equal. The different amount of heterogeneous catalyst is due to fact that the loading of the metal-Salen complex to the silica in case of the ester immobilization (0.01 mmol g^{-1}) is much less in comparison to the peptide case (0.16 mmol g^{-1}) (Table 1). Therefore, the difference in catalytic activity may be explained by strong diffusion obstacles for the reacting molecules to reach the active centers and for product removal from the silica pores. This is demonstrated in Fig. 4 by the inflection of curve **4b** in the first 10 h of the reaction.
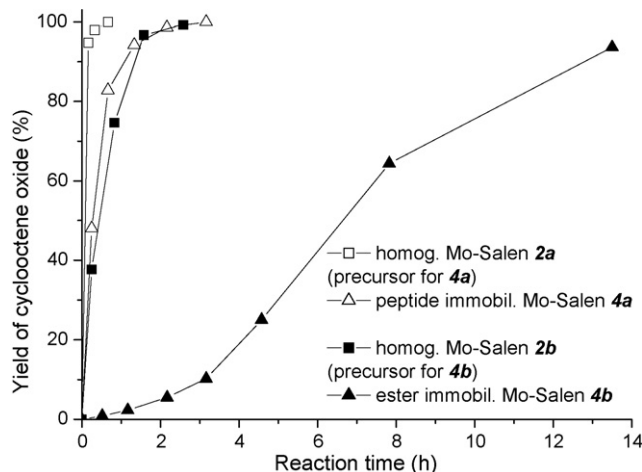

Fig. 4. Comparison of the catalytic activity of the peptide immobilized Mo-Salen **4a** with the ester immobilized Mo-Salen complexes **4b** in the epoxidation of cyclooctene at 75 °C with TBHP as oxidant. The metal content in the reaction mixture is equal.

3.5. Kinetic study of the epoxidation of cyclooctene

In this kinetic study the depletion of cyclooctene concentration in the presence of TBHP excess for different metal-Salen catalysts was monitored and plotted with respect to time. To calculate the rate constants the rate law expression for the epoxidation of cyclooctene may be written as [28]

$$\text{Rate} = k\left[\text{cyclooctene}\right]^{\alpha}[\text{TBHP}]^{\beta} \qquad (2)$$

and

$$\text{Rate} = -\frac{d(\text{cyclooctene})}{d(t)}, \qquad (3)$$

where [cyclooctene] and [TBHP] are cyclooctene and TBHP concentration, respectively, α the order of reaction with respect to cyclooctene, β the order of reaction with respect to TBHP, and k is the rate constant for consumption of olefin. In order to find α, the rate expression (2) may be rewritten as

$$\text{Rate} = k'\left[\text{cyclooctene}\right]^{\alpha}$$

if $[\text{TBHP}]^{\beta}$ = constant, because it is in excess.   (4)

Combining expressions (3) and (4) leads to

$$-\frac{d(\text{cyclooctene})}{d(t)} = k'(\text{cyclooctene})^{\alpha}. \qquad (5)$$

In case of $\alpha = 1$ by integrating expression (5) with assumption that the epoxidation runs at high selectivity and side reactions do not consume significant amount of olefin, the expression (5) can be written as

$$-\ln(1 - X) = k'(t), \qquad (6)$$

where X is the conversion of cyclooctene after time t and k' is pseudo-first-order rate constant.

The plot of $-\ln(1 - X)$ with respect to time for the consumption of cyclooctene during epoxidation in the range 45–70 °C with the homogeneous molybdenum-Salen complex **2b** in the
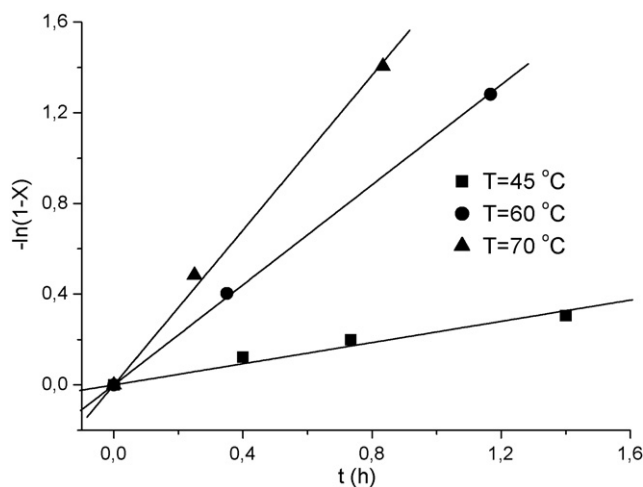
Fig. 5. Pseudo-first-order kinetic dependences for the consumption of cyclooctene during epoxidation at 45, 60 and 70 °C with the homogeneous molybdenum-Salen complex **2b** in the presence of excess TBHP.
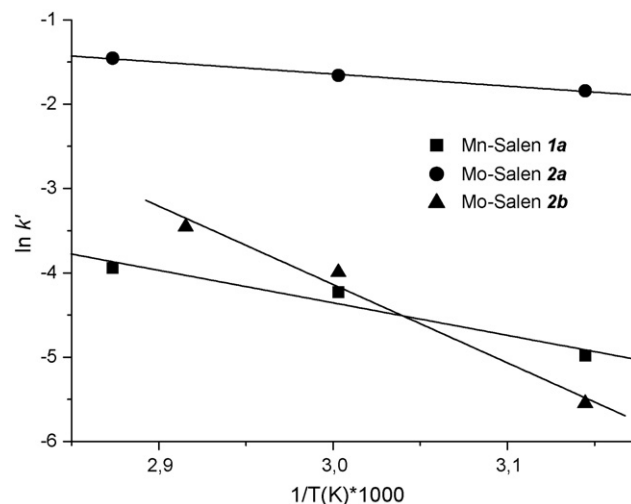

Fig. 6. Arrhenius plots of the pseudo-first-order rate constants of the cyclooctene epoxidation with homogeneous metal-Salen complexes **1a**, **2a** and **2b**.

presence of excess TBHP is given in Fig. 5. The values of the pseudo-first-order rate constants k' for the different homogeneous and heterogeneous catalysts at different temperatures are given in Table 2. The results show that in case of the homogeneous manganese-Salen complexes an increase of temperature raised the obtained rate constants while the epoxide yield is decreasing (Fig. 1). This proves the effect of high thermal and catalytic decomposition of the hydroperoxide. Comparison of the k's of homogeneous with heterogeneous metal catalysts at the same temperature demonstrates the decrease of the rate, which is caused by steric effects and diffusion in the pores.

To compare the catalytic activity of the metal-Salen complexes formed with different ligands (**a** and **b**, Scheme 1) the Arrhenius plot ($\ln k'$ versus $1/T$) was drawn (Fig. 6) and the value of the activation energy (E_a) was evaluated from the slop of the plot (Table 2). It can be seen that metal complexes with Salen ligands containing carboxylic group in its structure (**1a** and **2a**, Scheme 1) possess lower activation energy (32.1 and 11.6 kJ mol^{-1} for manganese and molybdenum complexes, respectively) in comparison with the sodium salt containing ligand **2b** (77.2 kJ mol^{-1}). The effect may be explained by the influence of acidic protons of carboxylic group of Salen ligand on the catalytic activity of transition metal.

3.6. Influence of protic agents

To prove the above assumption the influence of carboxylic group by addition of acetic acid was tested. It was also reported that the presence of organic acids, e.g. carboxylic acid, benzoic acid and its derivatives, or electron-withdrawing groups increased the activity of the iron [29] and the ruthenium [30] catalysts coordinated with Schiff base ligands during oxidation reactions. Thus, Legros and Bolm [29] demonstrated different influences of substituted benzoic acids on the sulfide oxidation. This effect can be explained by intramolecular interaction of the free carboxylic group with the Schiff base center, which increases activity of transition metal during the oxygen transfer from the oxygen source to the substrate. To understand the effect of the presence of acidic groups in more detail, catalytic experiments with acetic acid as an additive were performed at 60 °C, catalyzed by the homogeneous Mo-Salen complex **2b**. The molar ratio of acetic acid to olefin amounted to 0.07 and ca. 2.0, respectively. Moreover, a comparative experiment without acetic acid was carried out (Fig. 7).

The experiments gave complete conversion of olefin and demonstrated that the presence of acetic acid significantly accelerates the epoxidation rate. However, a further increase of the acetic acid concentration did not give positive effects. That is the

Table 2
Pseudo-first-order rate constants (k') and activation energy (E_a) of different homogeneous and heterogeneous catalysts in the epoxidation of cyclooctene with excess TBHP

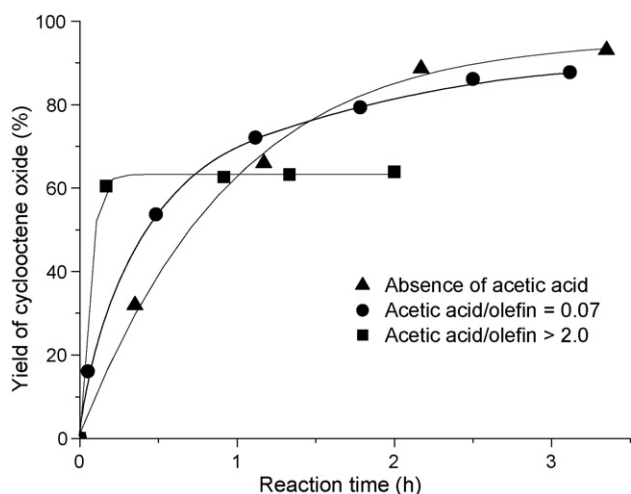| Catalyst	Rate constant, $k' \times 10^{-4}$ (s^{-1})				E_a (kJ mol^{-1})
	45 °C	60 °C	70 °C	75 °C	
Homogeneous Mn-Salen **1a**	1.2	2.4		3.2	32.1
Heterogenous Mn-Salen **3a**	1.1				
Homogeneous Mo-Salen **2a**	26.4	31.7		38.9	11.6
Homogeneous Mo-Salen **2b**	0.7	3.1	5.3		77.2
Heterogenous Mo-Salen **4a**			1.2	1.9	
Heterogenous Mo-Salen **4b**			0.06		

Fig. 7. The influence of acetic acid on the catalytic epoxidation of cyclooctene with TBHP catalyzed by the Mo-Salen complex **2b** at 60 °C.

result of a higher extent of side reactions in the acidic matrix, based probably on radical pathways.

3.7. Catalytic epoxidation with different olefins and oxidants

To compare the epoxidation of cyclohexene and cyclooctene, respectively, as olefins and TBHP and 30% of hydrogen peroxide in water, respectively, as oxidative agents, experiments were performed with the peptide immobilized Mo-Salen complex. The results are summarized in Table 3. The observed small difference in yield of cyclooctene and cyclohexene oxides at 60 °C is in accordance with literature results [4,26,31].

The significant difference in the cyclooctene oxide yield in case of using *tert*-butylhydroperoxide in comparison to water solution of hydrogen peroxide can be explained by an inhibition effect due to water presence and its additional formation during epoxidation in case of hydrogen peroxide. Although it is known that hydrogen peroxide as well as alkylhydroperoxides follows the same mechanism during epoxidation, hydrogen peroxide is rather not applicable because the water (30% aqueous

Table 3
Comparison of the catalytic activity for cyclohexene and cyclooctene, respectively, and with HP and TBHP, respectively, over the peptide immobilized Mo-Salen complex **4a**

Different reagents	Yield of epoxide (%)
Cyclohexene[a]	28
Cyclooctene[a]	33
TBHP[b]	62
HP[b]	23

[a] The reaction was carried out with TBHP at 45 °C during 26 h.
[b] The reaction was carried out with cyclooctene at 60 °C during 26 h.

solution of hydrogen peroxide) strongly inhibits the metal catalyst [32]. Moreover, the catalytic epoxidation with molybdenum catalysts using organic hydroperoxides as oxidant demonstrates higher activity due to the influence of alkylic group in comparison with hydrogen peroxide. Another significant reason for such inhibition with hydrogen peroxide water solution may be a strong coverage of the silica surface by water. This effect causes blocking of the pores; therefore, the access to the active catalytic centers is strongly hindered. The heterogeneous catalyst after epoxidation with hydrogen peroxide water solution could not be washed properly by most of the aprotic organic solvents because of its highly hydrated surface.

3.8. Reuse of spent catalyst

In case of the peptide immobilized Mo-Salen complex **4a** the persistence of the catalytic activity was checked for 10 consecutive runs in the epoxidation of cyclooctene at 75 °C. The results are summarized in Fig. 8, where it is seen that in the first run the immobilized catalyst exhibited a smaller activity in epoxide formation in comparison to the following runs. This must be due to a difference in activity of the initial state of the transition metal (e.g. Mo(IV)) in comparison to the state after the first run. It was observed that the dark brown color of the catalyst during the first hour of the first run was turning to a constant yellowish, indicating a change in oxidation state of metal (Mo(IV) → Mo(VI)). This may be the reason why the initial activity was higher in the second and following runs. The catalytic activity of
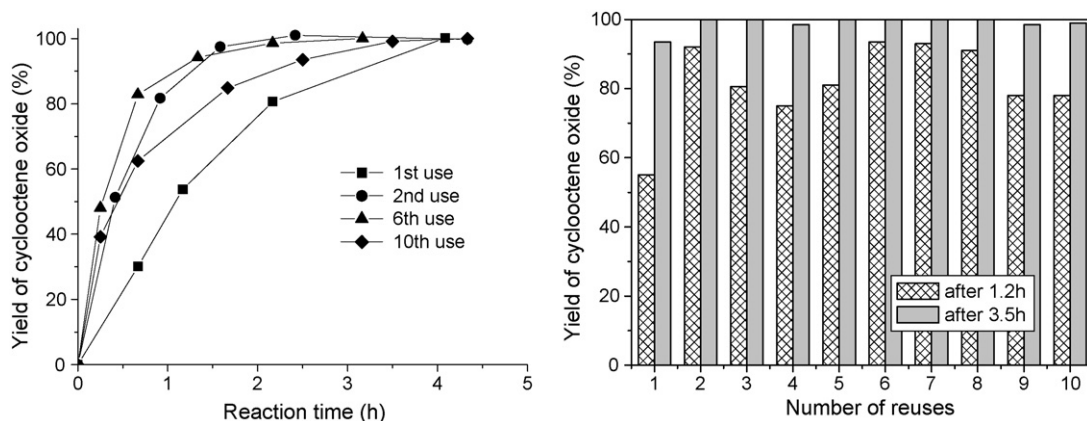

Fig. 8. The catalytic activity of the peptide immobilized Mo-Salen complex **4a** in 10 consecutive runs of cyclooctene epoxidation at the following reaction conditions: 1.7 mmol cyclooctene, 5.1 mmol TBHP, 0.015 mmol catalyst (active centers of metal) in 1.5 ml of the toluene as solvent at 75 °C.

Table 4
Reuse of the peptide immobilized Mo-Salen complex **4a** in 10 runs of cyclooctene epoxidation

Number of reuses	Yield of epoxide[a] (%)	TOF[b] (s^{-1})	Leaching of Mo-Salen[c] (%)
1	100	6.8×10^{-3}	4
2	100	1.3×10^{-2}	<1
6	100	7.8×10^{-3}	–
10	100	1.1×10^{-2}	0

[a] No significant amounts (<1%) of other products were determined. Yield of epoxide (%) was based on initial amount of olefin.

[b] TOF (turnover frequency) = moles of produced epoxide/(moles of catalyst × reaction time in seconds).

[c] Leaching of Mo-Salen in the reaction mixture at 75 °C determined after cyclooctene epoxidation. The values presented are in mole percent of leached amount to the initial amount of molybdenum in the silica.

the spent catalyst in the consequent uses was very similar. This proves the stability of the obtained immobilized metal-Salen complexes towards solvents, water presence as well as oxidative agents (TBHP, HP). Moreover, the immobilized Salen complex is resistant against leaching of Salen molecules (Table 4).

4. Conclusion

The epoxidation of cyclooctene and cyclohexene with *tert*-butylhydroperoxide and hydrogen peroxide catalyzed by homogeneous as well as immobilized peptide and ester bound Mn(III) and Mo(IV)-Salen complexes was investigated in the temperature range 45–75 °C. The transition metal-Salen catalysts may initiate the following processes:

(1) epoxidation of the olefin yielding the epoxide;
(2) radical decomposition of TBHP by the Haber-Weiss reaction mechanism;
(3) side reaction, e.g. ring epoxide opening and further oxidation.

The results demonstrate that the epoxidation occurs for homogeneous and immobilized manganese and molybdenum catalysts, however, in case of molybdenum the epoxidation process shows a higher selectivity to epoxide (>97%) in contrast to manganese where the second type of reaction, i.e. the decomposition of TBHP is the main reaction. The third type of reaction was not observed for both metals.

The recycling experiments and also the catalytic reactions at different temperatures confirm the high stability of the obtained anchored manganese and molybdenum-Salen complexes at least up to 75 °C, towards different solvents (polar, nonpolar) and water presence as well as oxidative agents (TBHP, HP). The heterogeneous Salen catalysts show high resistance against leaching and in the case of molybdenum were used for 10 consecutive runs without significant loss in activity (after the forth run the presence of molybdenum in the reaction solution was no longer detected). The kinetic study showed that the increase of temperature leads to an increase in the epoxidation rate. Heterogeneous catalysts exhibit lower catalytic activity in comparison to homogeneous analogues due to steric effects and diffusion hindrance inside the silica pores.

It was shown that the presence of free carboxylic group in the homogeneous metal-Salen complex or addition of acetic acid increases catalytic activity of metal-Salen complexes in the epoxidation of olefins.

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