



Editor's choice paper

The enantioselectivity of the manganese–salen complex in the epoxidation of unfunctionalized olefins and the influence of grafting



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ABSTRACT

Jacobsen's complexes are famous for their usability for enantioselective epoxidations. However, the applicability of this catalytic system has been severely limited by several practical problems such as deactivation and separation after reaction. Grafting of Jacobsen-type complexes on solid supports is an attractive way to overcome these problems but led to a decrease in selectivity. A combined theoretical and experimental approach is presented to unravel the factors governing enantioselectivity. The importance of different substituents was determined by analyzing the transition state for the oxygen transfer using the full system as a model. An analysis of the asymmetric complex has shown an inherent tendency for a decreased selectivity due to the lack of specific bulky groups. Experimentally an immobilized Jacobsen catalyst on a metal organic framework (MIL-101) was synthesized which confirms the computational tendencies but the decrease in selectivity is limited, indicating that the MIL-101(Cr) is a suitable carrier for this complex.

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1. Introduction

Reactive chiral products are of great value in the chemical industry [1–3]. Many commercial products contain some sort of chiral center and the production of these can be facilitated by readily accessible chiral intermediates. One compound that can serve as such an intermediate is a chiral epoxide. These compounds are very reactive due to the epoxide ring and the chirality can be transferred to further products.

Given the synthetic value of chiral epoxides many catalytic systems have been developed to produce these compounds with high selectivity, with the titanium tartrate catalyst [4–10] and the chiral metal–salen complex [11–16] as the most well-known. The latter complexes, originally designed by Jacobsen and Katsuki, are highly performing in the epoxidation of unfunctionalized olefins. With optimized conditions, olefins such as styrene [16] and chromene derivatives [14] could be epoxidized with high (>85% ee) selectivities. Different oxidizing agents can be applied with the catalytic system,

for example NaOCl in aqueous media or meta-chloroperoxybenzoic acid in organic solvents.

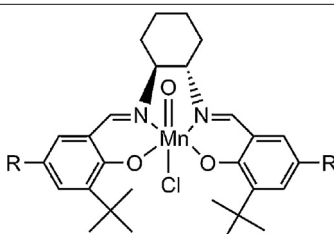
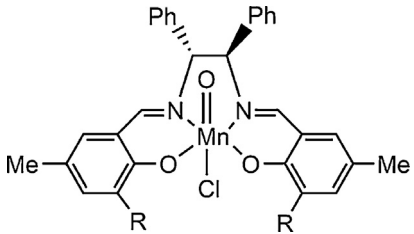
Despite their large applicability and commercial availability the mechanism that controls the enantioselectivity is not thoroughly understood. Several experiments have been conducted to probe the approach vectors [13,14,17] (Table 1). From a computational approach numerous ab initio studies on the mechanism of oxygen transfer using a smaller model for the Jacobsen catalyst [18–21] have been performed. Linde et al. [22,23] acknowledged early on that the choice of a different spin state (spin 0,1 or 2) has a huge influence on the resulting reaction mechanism. They proposed the existence of different intermediates depending on the spin state of the complex. Cavallo et al. [24,25] further investigated this phenomenon and noticed the importance of the choice of the right DFT functional. Their research allowed for the proposition of a catalytic cycle for the epoxidation using sodium hypochlorite [20]. However next to these studies on the mechanism of oxygen transfer, the research on the selectivity has always been performed with molecular mechanics methods [19]. To obtain a full understanding of all interactions contributing to the overall selectivity it is recommended to model the complete catalyst at a higher level of theory. Such studies have now become feasible with current computational resources.

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Table 1
Selectivity of salen-type catalysts bearing different substitutions in the epoxidation of methylstyrene [13,14].

Catalyst	Substituents	%ee
	R = Me R = tert-butyl	80% 92%
	R = H R = tert-butyl	0–3% 81%

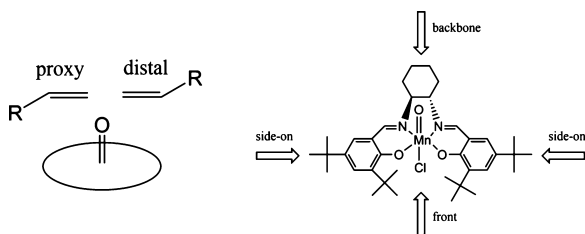


Fig. 1. Schematic representation of various approach vectors to the salen complex, adapted from Fristrup et al. [17] and Jacobsen et al. [19].

Experiments with styrene derivatives featuring different substituents [17] have led to the conclusion that the so called distal, side-on approach (schematically shown in Fig. 1), where the substrate approaches from the side and the most bulky group is pointed away from the complex is preferred, except for some tri-substituted variants. However, an experiment where different substituents were introduced on the salen ligand [14] seemed to point to an approach via the backbone (diamine). The molecular mechanics study allowed to identify different possibilities for the approach but, due to the use of classical force fields, no transition states could be considered. Therefore no conclusion on the influence of the transition state on the selectivity could be drawn. Regardless of these previous studies, the most important feature of a salen type complex with a diaminocyclohexane backbone appear to be the substituents on the 3/3' positions as schematically shown in Fig. 2. In the absence of bulky groups at these positions all selectivity is inhibited [13]. The substituents on the 5/5' positions [14] also have an influence on the resulting selectivity but the above mentioned studies could not provide a rationale for this observation

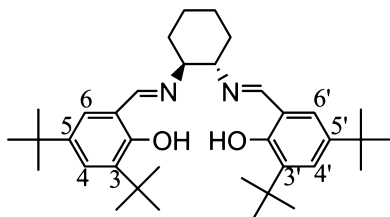


Fig. 2. Symmetrical salen ligand with a diamine backbone and the numbering of the substituents.

In this paper we provide an in depth study on the selectivity of the salen complex by localizing the transition states of various approach modes using a density functional theory (DFT) methodology in which the full catalyst complex is taken into account. This is, to our knowledge, the first time a DFT methodology is applied on the Jacobsen complex without simplification of the complex by omitting functional groups or larger parts of the complex. A report by Morokuma et al. [26] already showed the importance of including the salicylaldehyde parts in the model, but the inclusion of functional groups on these moieties will further improve the results. Both symmetrical and asymmetrical salen complexes will be investigated to get an in-depth view on the effect of substituents at various positions of the ligands on the selectivity. This is important when considering the effect of the covalent grafting of salen-type complexes, where an asymmetric substitution is often used to bind the complex to a support [27–29]. Such grafting procedures, or in general the immobilization of the homogeneous system into a heterogeneous system might be beneficial. Similar to many other homogeneous catalysts, the separation of the complex after reaction is a significant bottleneck for its applicability. Moreover, manganese-salen type complexes undergo deactivation via an irreversible stacking of the oxidized species, impeding their long-term use. The most effective way to optimize the catalyst is the immobilization of the homogeneous system on a solid support that impedes any stacking and facilitates the separation of the catalyst. On the other hand care needs to be taken in how far such procedure maintains the original high selectivity of the homogeneous system. In an earlier study [30] of the present authors a heterogeneous system was developed by the encapsulation of the Jacobsen complex in the pores of a metal organic framework. This immobilization omitting, all covalent bonds, resulted in a material that maintained the selectivity of the original catalyst. This could be explained by simulations of the epoxidation reaction where it was shown that the transition state governing the selectivity fitted perfectly in the cage of the host structure.

In this study we will assess the effect of a grafting procedure of the salen complex on its selectivity. The host material for the grafting procedure is the metal organic framework (MOF) MIL-101 [31,32]. This material has been chosen for the high stability in the various media that are used in the postmodification process. There have been various studies where the salen complex was immobilized on different supports [28,29,33–35]. This mostly led to a decrease in selectivity unless there was no covalent interaction between the complex and the host, allowing a high freedom of movement [30]. One possible approach to immobilizing the complex is building it up piece by piece on the solid support, as reported by Angelino et al. [28,29] In this paper a similar approach is used anchoring the catalyst on a chloromethylated MIL-101.

2. Computational and experimental methods

2.1. Reaction mechanism and models used for the catalyst

In an earlier study we have proven that by using the full salen complex as a model (Fig. 3(a)) the different approach vectors leading to the various enantiomers could be found. In addition, the difference in free energies between the various transition states were able to explain the observed selectivity of the catalyst [30]. In order to obtain a sufficient amount of detail, the full catalyst was used as a model, since any simplification would risk the loss of critical information on the steric influence. It was also shown that the calculations on the homogeneous system were able to rationalize also the observed selectivities for the same catalyst which was embedded in the NH₂-MIL-101(Al) system. In this paper we use the same model system for the computational study but both symmet-

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