Unraveling the mechanism of the manganese-salen epoxidation

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Chiral salen-type complexes are valuable catalysts for the enantioselective epoxidation of unfunctionlized olefins. The mechanism of this reaction with the manganese-salen complex has always been the subject of an intense debate [1, 2]. The originally proposed mechanism featuring a radical intermediate seems to fail in explaining several experimental observations[3] and various alternatives have been proposed. However the obtained results were highly dependent of the chosen methodology.

We will present a methodological study comparing a broad range of DFT functionals with high-level CASSCF calculations [4]. An OPBE functional was shown to be the most performant. Using this functional it is confirmed that the mechanism featuring a radical intermediate is indeed the most likely. Moreover it makes it possible to explain the experimental observations that did not fit in the classical model. For example olefins with a cyclopropane moiety next to the double bound result in a mixture of epoxides and ring-opening products depending on the exact reaction conditions. Our calculations show that a radical reaction intermediate can lead to the observed product distribution. This methodology can thus prove to give more insights in the mechanism of this interesting catalyst, allowing it to be optimized further for numerous applications.

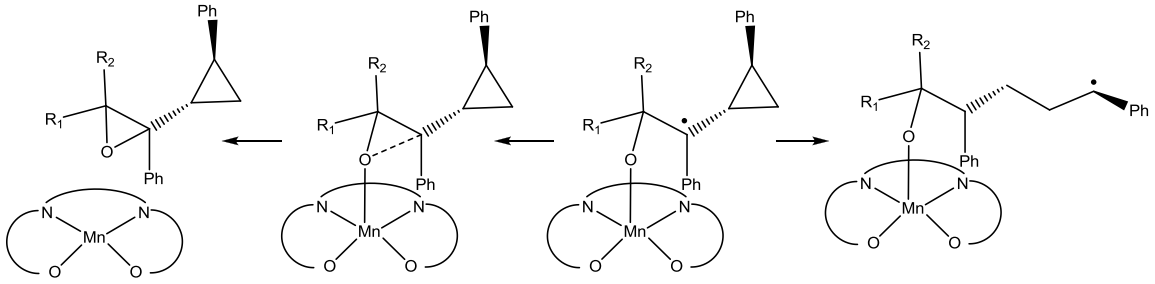

Figure 1 Possible reaction scheme with a cyclopropane containing olefin

[1] Cavallo, L.; Jacobsen, H., *Eur. J. Inorg. Chem.*, (2003), 892.
[2] Linde, C.; Akermark, B.; Norrby, P. O.; Svensson, M., *J. Am. Chem. Soc.*, (1999) **121**, 5083.
[3] Linde, C.; Arnold, M.; Norrby, P. O.; Akermark, B., *Angew. Chem.-Int. Edit. Engl.*, (1997) **36**, 1723.
[4] Sears, J. S.; Sherrill, C. D., *J. Chem. Phys.*, (2006) **124**, 144314.