Theoretical investigation of the demethylation of acetic acid

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1 Introduction

The DFG Research Unit 763 "Natural Halogenation Processes in the Environment- Atmosphere and Soil" has been carrying out research projects in the field of halogenated organic compounds. Recent soil samples from Australia point to a natural production of chloromethane in salt lakes. The iron-catalyzed oxidation reactions of organic material was investigated. For this purpose, various analytical methods (GC-FID, GC-MS, IC) were used. Furthermore, quantum mechanical calculations were performed to find reaction intermediates and to investigate the reaction mechanism.[1]

2 Computational Methods

In this project, complexes of Fe^{IV} and bispidine[2,3] based ligands $L^{1\text{-}4}$ were investigated as catalysts for the reaction with acetic acid (Fig. 1). The DFT calculations (Functional B3LYP[4]; Basisset def2-tzvp[5,6]; PCM-Model (solvent = Water)) were performed with Gaussian09[7].

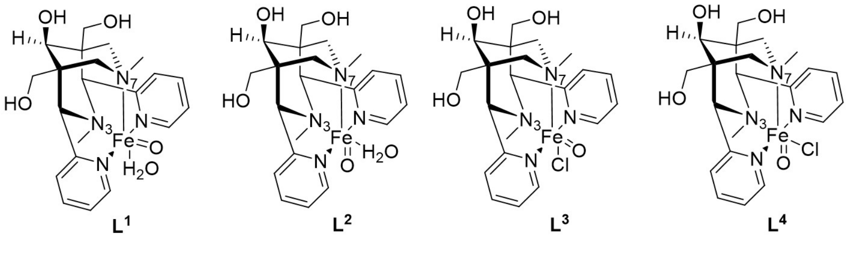

Figure 1: Fe^{IV} complexes of ligands L^1, L^2, L^3 and L^4.

3 Results

The Fe^{IV} complexes have two important spin states (Fig 2.). Therefore the complexes were optimized in S=1 and S=2 multiplets to find the estimated ground state. The iron(IV)-oxo bispidine complexes were analyzed by their energy, bond lengths, charges and spin densities.

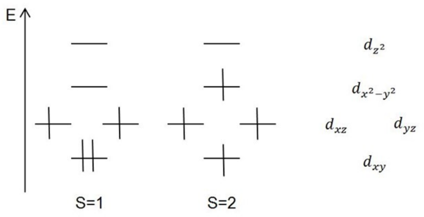

Figure 2: Spin states of the investigated iron$^{\mathrm{IV}}$ complexes.

L^1 and L^3 have the lowest ground state energies. The difference in the bond length is significant. Every coordination bond in the chloro complex is longer than in the water complex. Furthermore, experimental results show, that the water-complex plays the important role in the reaction mechanism. Therefore the transition states and products were analyzed for the reaction of L^1 with acetic acid. Two different types of reactions were examined. One is the C-H activation of the methyl group of the acetic acid and the other one is the oxidation of the carboxylic group. When comparing the two different spin states on the reaction coordinate (Scheme 1), it is remarkable that the energy barrier of the high spin complex is almost half of the low spin complex. Therefore it is likely that the S=1 state switches to the S=2 state and then activates the C-H bond.

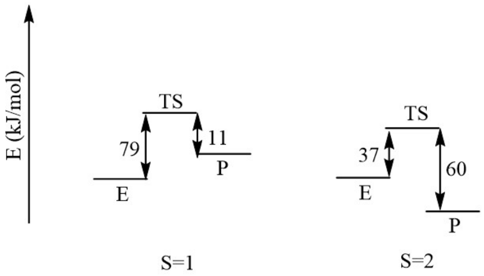

Figure 3: Reaction coordinate of the H-Atom abstraction by L^1. (E = educts, TS = transition state, P = products)

The attack of the carbonyl group is very energetically unfavorable. When comparing the energy barrier between the C-H activation (Scheme 1) and the attack of the C1-Atom (Scheme 2), one can see a large difference in the activation barriers.

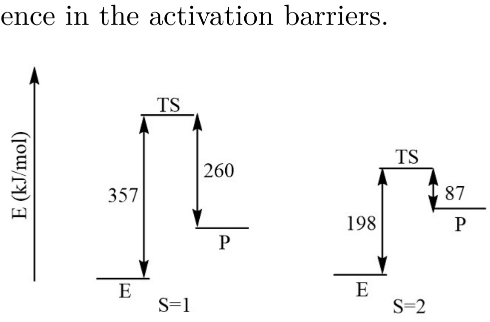

Figure 4: Reaction coordinate of the C-Atom abstraction by L^1. (E = educts, TS = transition state, P = products)

4 Conclusions

In this work Fe^{IV} bispidine complexes have been examined for their activity in the reaction with acetic acid. The iron(IV)-oxo complex L^1 acts as a catalyst in the activation of the C-H bond and possibly as an oxidant for the carbonxylic group. So far, there is no experimental proof of the intermediates. Further spectroscopic studies (EPR, stopped-flow of the intermediates) are inevitable for a deeper insight into the mechanism. This will be supported by further (DFT) quantum chemical calculations.

Acknowledgements

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