

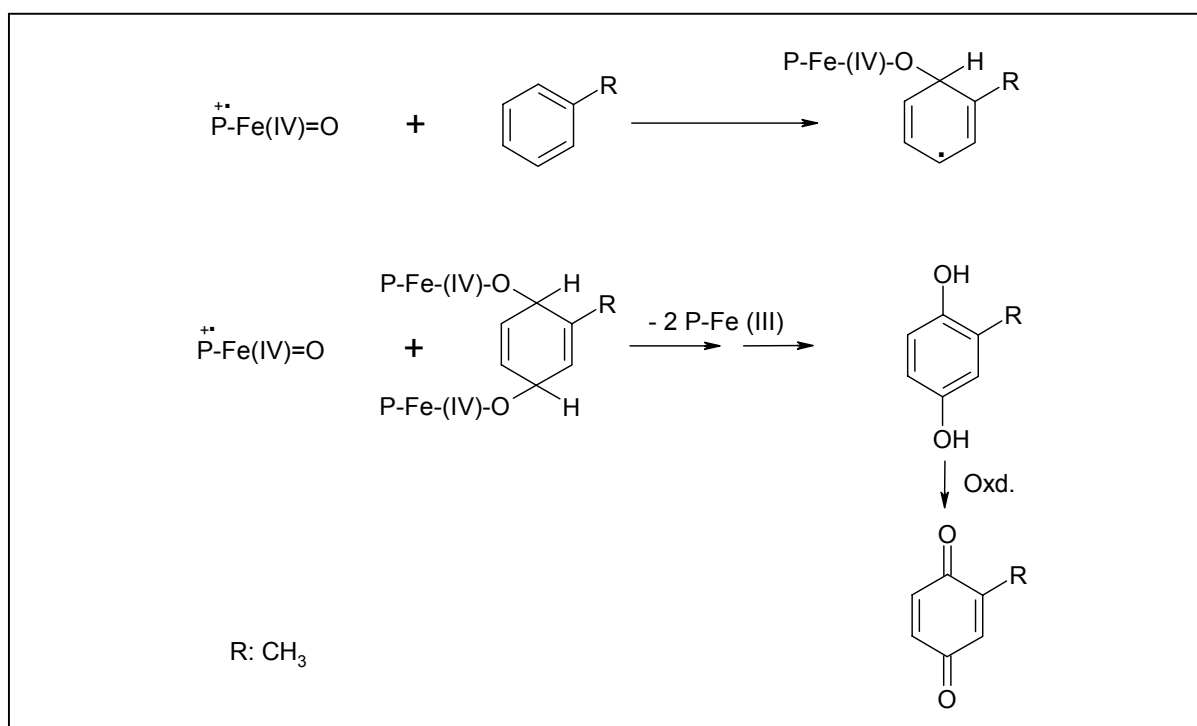
## 13 Summary

The main objective of this work was to investigate if it would be possible to oxygenate simple non activated hydrocarbons by using biomimetic model compounds. For these reactions we tried the approach in using model compounds for cytochrome P<sub>450</sub>, such as tetraphenylporphyrins of transition metals like iron and manganese as central ions instead of the iron chelate in cytochrome P<sub>450</sub>.

Investigating these systems, a biomimetic reagent system should be developed which is suitable for the determination of components of gas and vapor samples especially for the definition of partly inert or slowly reacting organic hydrocarbons like benzene and up to short linear alkanes like butane.

This proposed biomimetic system should be characterized by mild reaction conditions, i.e., it should be able to work at room temperature and without additional chemically corrosive auxiliary reagents, as well as to react spontaneously which means to show good results in short reaction times.

Using these systems, it was investigated in the first part of this thesis, whether it is possible to oxygenate toluene and benzene.



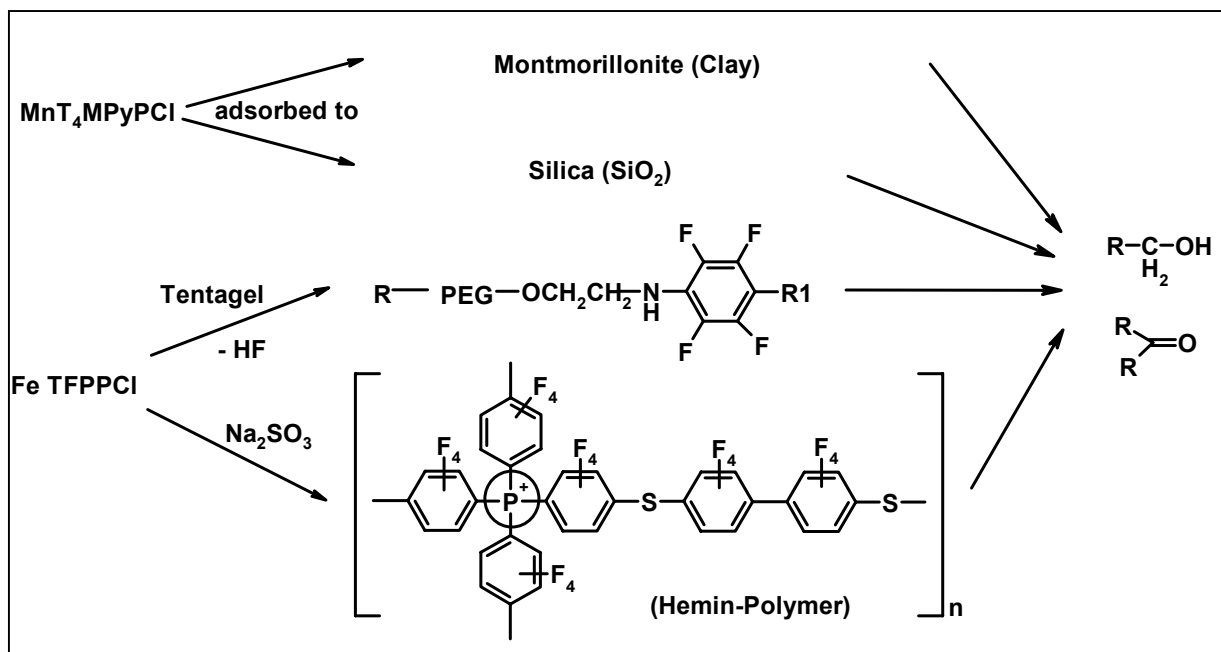
**Scheme 13.1** Mechanism of the formation of 1,4-Benzoquinone

After optimization of the reaction system, we succeeded in the oxygenation of toluene as well as benzene using a two-phase system. Thereafter a one-phase system has successfully been implemented; and finally a reaction in the gaseous phase has also been realized, allowing to make use of this kind of biomimetic reactions even in test-tubes.

By variation of the components of the reaction mixture a reaction of the substrate was achieved which occurred spontaneously. Furthermore the transition of benzene to 1,4-benzoquinone out of the gaseous has been demonstrated in a test tube. During further experiments we investigated if these systems also show efficient reactivities concerning the use of these systems adsorbed on different matrices. It could be shown that the reactivity was not influenced by the adsorption of the reaction mixture to the support.

In the further course of this work, we concentrated on the investigation of the oxygenation of aliphatic hydrocarbons aiming at the oxygenation of methane. A first series of experiments using the well known system did not lead to positive results. Even when using highly sensitive analysing test-tubes no metabolites of methane could be detected and analysed. So during further experiments the emphasis was put on the approach from long-chain to short-chain aliphatic hydrocarbons.

The reactions systems, successfully used as described above, did not lead, however, to reproducible results. To solve the basic analytical problems, which we faced here, we decided to use immobilisation of the metalloporphyrins on inorganic supports.



**Scheme 13.2** Immobilized porphyrin catalysts

Therefore different immobilized/supported porphyrin catalysts have been synthesized. After polymerization, intercalation in clays, adhesion at and adsorption to different supports, potent systems have been developed, which allow the oxygenation of low reacting molecules such as alkanes up to gaseous butane and also toluene and benzene. Alkanes resulted in the hydroxylated products respectively the corresponding carbonyl structures, from toluene and benzene we obtained the accompanying 1,4-quinones.

The systems as described combine many advantages, such as a very simple preparation and an easy recovery with the quality to be potent oxidation catalysts.

An application of the described immobilized catalysts during further biomimetic reactions, mimicking the cytochrom P<sub>450</sub>-system seems to be highly promising.