Review on the PhD dissertation of Mrs. Szabina Papné Goger entitled: Synthetic Fe- and Cu-containing 1-aminocyclopropane-1-carboxylic acid oxidase models

It is the case when the situation of the reviewer is easy and complicated at the same time. It is easy because I was one of the reviewers who prepared the preliminary report, and complicated because my former suggestion were considered, the author considerably modified the dissertation.

The dissertation is based on three publications appeared in high-impact factor journals (in two of them Mrs. Papné is the first author) and nine conference lectures. If I want to characterize the dissertation I say it concise, it is just 73 pages with 21 pages appendix. The theses is well-prepared, well-written in good style, it contains 94 literature citations and a good survey of the relevant publications.

The subject of the manuscript is enzymatic reactions. In the literature survey part of dissertation the author describes the main types of enzymatic reactions and shows that the research in this field is of outermost importance because of the demand for understanding the biochemical processes taking place in living organisms, and also because of the technological applications of enzymatic reactions.

The simplest hormone that forms in enzymatic reactions is ethylene. The dissertation of Mrs. Papné deals with the last steps of the ethylene forming reactions. This simple hydrocarbon serves as a plant hormone regulating the ripening process in fruits and vegetables. The ethylene in the plants is synthesized by 1-aminocyclopropane-1-carboxylic acid oxidase (ACCO) enzyme. This enzyme – as most enzymes – is a high molecular weight molecule which makes the investigations of enzymatic reactions rather expensive and complicated. In the theses Mrs. Papné prepared and characterized new catalysts that mimic the function of ACCO.

The author prepared Fe^{III}(SALEN)Cl complexes (SALEN, *N*,*N*-bis(salicilidene)ethylene diamine), Cu^{II}(amino acid) complexes and Cu^{II}-bipyridine (bpy) complexes and characterized their properties and oxidation reactions.

It is important to emphasize that the author in the laboratory work applied a very wide variety of experimental techniques, such as UV-Vis, FTIR and ESR spectroscopies, Roentgen diffraction, cyclic voltammetry, GC separation with product identification and also solution isotope effect investigations. The laboratory results were supplemented also by theoretical calculations.

In Section *4.1 Investigation of [Fe^{III}(SALEN)Cl]* Mrs. Papné investigated the oxidation reactions of SALEN complexes using different oxidants, (H_2O_2, PhIO, TBHP, MCPBA and PMS). H_2O_2 was found to be a good oxidant and it was used in the further studies. Based on the experiments with 8 (cyclic and acyclic) amino acids by measuring the conversion, TOF (turnover frequency) and solvent isotope effect the author concluded that the reaction takes place with proton transfer-electron transfer mechanism as rate determining step. There is a stepwise sequence of reactions. The catalyst concentration is about three orders of magnitude smaller than the substrate and the oxidant concentrations. It would be interesting to know how much changes take place in the activity of the catalyst. In other words how stable is the catalyst in these reactions.

The Section *4.2 Cu-containing amino acid models* starts with X-ray, IR and cyclic voltametric characterization of the isolated/prepared complexes. The author gives detailed calculations of bond angle and bond length values for the solid complexes. In the reactions performed with [$CuCl_2$] and [Cu^{II}(AA)$_2$] complexes just slight differences were found in the calculated turnover frequencies indicating an identical active form.

Amino acid complexes with bpy ligand were found to be good models of the enzymatic system due to the efficient reaction and the similar product formation. During the reaction a geometric change is suggested in the catalyst from square pyramidal to tetrahedral due to an oxidation change from Cu^{II} to Cu^{I} oxidation state.

The author has divided to 6 theses her main results. 1 and 2 are connected with the Fe^{III}(SALEN)Cl complexes. Mrs. Papné suggests a high-valent (Fe^{IV}) oxo centre in the intermediate and assumes a pre-equilibrium between the substrate and the catalyst.

Points 3-6 refer to Cu^{II} complexes. Both the amino acid and bpy complexes were found to be good structural and functional models of ACCO. The catalytic activity is rationalized with a possible geometric change from square planar to tetrahedral accompanied by an oxidation state change from Cu^{II} to Cu^{I}.

These theses well represent the main results of the dissertation and I accept all of them as new results.

Summarizing my opinion: Mrs. Papné based on high-level experimental work has prepared an imposing PhD dissertation with significant results in the field of enzymatic reactions. I suggest to defend the theses in a public debate, and in case of successful defending to give the PhD title to Candidate.

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