MASARYK UNIVERSITY
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Brno, Jan 27, 2018

Referee Report for the PhD Thesis of Ing. Erik Andris

entitled "Investigation of Non-Heme Iron-Oxo Intermediates in the Gas Phase"

The dissertation work of Ing. Andris provides research results aimed to design methods to study iron-oxo complexes in the gas phase for the field of biomimetic chemistry, and to establish the spectroscopic and chemical correlations between chemical processes occurring the gas phase and the condensed phase.

The thesis contains a large amount of original and very interesting both experimental and calculation results and shows a notable depth of scientific details and understanding. In general, the text is formally well organized and written in an eloquent and logical style. The English is idiomatic and clear, I found only minimum marginal and formal errors.

The text is divided into five chapters. The first chapter, Introduction, acquaints the reader with the necessary background, such as chemistry and occurrence of iron atom-containing enzymes and reported iron-oxo model complexes, and the corresponding MS studies used to study those species. The second chapter, Material and Methods, not only gives the fundamental experimental details but also describes and explains the basic principles of the instrumentation used in his work. The next two chapters provide the reader a comprehensive information about two broader projects studied under the tutelage of Prof. Jana Roithová: IRPD spectroscopy investigations of iron(IV)-oxo complexes and iron(III)-oxo complexes in the gas phase with an established interlink between the gas and condensed (solution) phases. These parts contain a large amount of original and state-of-the-art results and display erudite, professional and sophisticated combination of experiment and theory. The thesis shows a noteworthy depth of understanding. It is noted that the results described in this thesis have already been published in three highly-impacted journals. The last chapter contains concluding remarks.

Here, there are several questions which may deserve the discussion during the thesis defense.

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- Helium was used as a tag in the described IRPD analyses because it manifests very small binding energies with substrates. Is it always an advantage? Could a site-selective binding (to the substrate) be of any interest for future structure analyses?

- Could an atom such as Ar in those association complexes act as a heavy atom to trigger spin change, for example, in a triplet state complex? What is the lifetime of those weakly bound complexes?

- When an intramolecular kinetic isotope effect (HAT/DAT) was measured for the reaction of 1,4-cyclohexadiene-1,2,3,4,5,6-d_6 (vs. a non-deuterated cyclohexadiene) was used (page 67), how the actual KIE is interpreted, if both H and D atoms from one cyclohexadiene molecule are available for the reaction? This would obviously not be the case of a hydride/deuteride transfer.

- The next question is related to highly exothermic processes (e.g., OAT), for which kinetic isotope effect does not have to be pronounced/observed even if the reaction step is rate-determining. Did the author consider this possibility?

- Page 95: "… may be caused by interfering association reaction with a KIE 1." Does this imply that PT-ET process is not the rate-determining step anymore?

In conclusion, I can state that this excellent dissertation work clearly merits the highest acknowledgment. I am pleased to give a full support to the thesis application of Ing. Erik Andris, and I propose that the **thesis is accepted without reserve**.

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