THESIS

THE PARTIAL OXIDATION OF UNSATURATED HYDROCARBONS WITH H_2O_2 OVER TS-1 INVESTIGATED BY ONIOM METHOD: FORMATION OF ACTIVE SITE AND REACTION MECHANISM

WEERAYUTH PANYABURAPA

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Science (Chemistry)
Graduate School, Kasetsart University
2006

ISBN 974-16-2371-2

Weerayuth Panyaburapa 2006: The Partial Oxidation of Unsaturated Hydrocarbons with H_2O_2 over TS-1 Investigated by ONIOM Method: Formation of Active Site and Reaction Mechanism. Master of Science (Chemistry), Major Field: Physical Chemistry, Department of Chemistry. Thesis Advisor: Professor Jumras Limtrakul, Ph.D. 75 pages.
ISBN 974-16-2371-2

The mechanism of alkene oxidation with hydrogen peroxide over the defect titanium silicalite-1 (TS-1) was investigated at the density functional theory using the 9T B3LYP/6-31G(d,p) cluster and the two-layered 9T/65T ONIOM(B3LYP/6-31G(d,p):UFF) cluster scheme. The titanium hydroperoxo intermediate in bi-dentate manner, Ti(η^2-OOH), occurring through the single-step double proton transfer mechanism with the assistance of a neighboring silanol group, was proposed to be an active species in the oxidation process. This species was found to be susceptible to the number of water molecules surrounding the active region. The introduction of an additional water molecule into the hydrated Ti(η^2-OOH) complex results in the formation of titanium peroxo species, Ti(η^2-OO$^-$), in accordance with the role of water in hydroperoxo-peroxo interconversion in the TS-1/H_2O/H_2O_2 system. The oxygen abstraction step in the epoxide formation was found to be the reaction rate determining step, and was sensitive to a number of methyl groups substituted to the active C=C bond of alkene molecules. The 30T/65T ONIOM2(B3LYP/6-31G(d,p):UFF) apparent activation energies for ethylene, propylene, and *trans*-2-butylene were estimated to be 15.5, 13.6, and 12.2 kcal/mol; respectively, in agreement with the reactivity series of the gas phase calculations and comparable with available experimental apparent activation energy of 1-hexene of 15.5±1.5 kcal/mol.

Student's signature Thesis Advisor's signature ___ / ___ / ___

ACKNOWLEDGEMENTS

I would like to express my gratitude to the following people without whom I never would have been completed this thesis.

First, I would like to thank my supervisor, Professor Jumras Limtrakul, for his unwavering support and continuously valuable guidance throughout the study and research. He has provided advice, criticism and unfailing encouragement whenever needed since I started my program at Kasetsart University. I’m very honored to be his student. I also thank my committee, Assistant Professor Piboon Pantu and Associate Professor Cholticha Noomhom, and for their worthy suggestions.

It is a pleasure to acknowledge those who have supported me in various ways. All of my colleagues at LCAC; without them, it would have taken far longer to complete this thesis. A special thanks to all of my friends at the LCAC for your thoughtful help and support, which were always appreciated.

The financial support from the following is acknowledged with gratitude: The Higher Education Development Project Scholarship (MUA-ADB funds) Postgraduate Education

The generous availability of computing time by the Laboratory for Computational and Applied Chemistry (LCAC), Kasetsart University, is also gratefully acknowledged for research support.

Finally, I would like to dedicate this thesis to my dad and my mom. Their love and support for me is priceless.

Weerayuth Panyaburapa
April, 2006