Chapter 1 : Goldsmith Lab - Computational Catalysis and Materials

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Molecular mechanics 11 The previous section has described how one can compute accurately a system of about 30 atoms including one transition metal. The problem is, as mentioned above, that these are usually not the real catalysts, but model systems where the bulky substituents have been replaced by hydrogen atoms. Calculations on model systems are usually at least indicative of the nature and the energy barriers of the steps involved in a catalytic cycle, but they are often unable to provide information on some of the most interesting features, namely enantioselectivity and regioselectivity. The reason for this failure is simply that selectivity is often associated to the presence of the bulky substituents which are deleted when defining the model system. The correlation between bulky substituents and stereoselectivity is graphically shown in Figure 3, depicting the possible transition states in the dihydroxylation of a monosubstituted olefin by osmium tetroxide derivatives. This reaction is known to be selective [54], and the selectivity depends on whether the olefin substituent takes a position of type A or B in the transition state. The problem with calculations on a model system where the bulky base is replaced by is that the positions A and B are completely symmetrical, and thus, they yield the same energy. In other words, the reaction would not be selective with this model system. Molecular mechanics is a simple "ball-andspring" model for molecular structure. Atoms balls are connected by springs bonds , which can be stretched or compressed with a certain energy cost. The energy expression for molecular mechanics has a form of the type shown in equation 6, where each term is a summation extended to all atoms involved. The size of the atoms and the rigidity of the bonds, bond angles, torsions, etc. Electrons are not part of the MM description, and as a result, several key chemical phenomena cannot be reproduced by this method. Nevertheless, MM methods are orders of magnitude cheaper from a computational point of view than quantum mechanical QM methods, and because of this, they have found a preferential position in a number of areas of computational chemistry, like conformational analysis of organic compounds or molecular dynamics. The application of molecular mechanics to transition metal systems is not as straightforward as in the case of organic systems because of the much larger variety of elements and atom types and the relative scarcity of experimental data to which parameters can be adjusted. Significant progress has been made in recent years [], though its application to reaction mechanisms remains seriously complicated by the difficulty in describing changes in the coordination environment of the metal, and in locating transition states. Despite their limitations, MM methods have been applied to homogeneous catalysis, and a recent review collects more than 80 publications on the topic [61]. The problem of the structure around the transition metal was solved by taking the results of QM calculations on model systems or by choosing structures from X-ray diffraction. We consider that the application of standard force fields to homogeneous catalysis continues nowadays to be useful for preliminary qualitative descriptions, but that for a more quantitative description within the MM method one must necessarily go to the design of a specific force field for a Computational Methods for Homogeneous Catalysis 13 given catalytic process, the so called "QM-guided molecular mechanics" Q2MM [68]. In this approach, a specific force field is defined for a particular reaction, using all available data from experiment and data obtained from accurate QM calculations of minima and transition states. The definition and testing of the parameters is usually quite time consuming, but once the process is done for a particular reaction, the effect of small variations in catalyst or substrate can be computed with a very low computational cost. This quite recent method has been applied succesfully to processes of asymmetric synthesis [69] and catalysis, in the case of dihydroxylation [70]. The description of pure molecular mechanics MM methods presented in subsection 4. The logical solution to this complementary limitations is to divide the chemical system in two regions, and to use a different description for each of them, QM for the metal and its

environment, MM for the rest of the system. The total energy is thus the addition of three terms, the first one describing at a QM level the interactions within the QM region, the second one describing at an MM level the interactions within the MM region and the third one describing the interactions between the QM and the MM regions. The detailed form of this third term is not defined a priori, although it will be in principle composed of a QM and an MM description, as shown in equation 8, where the term can be roughly related to electronic effects and the term to steric effects [71]. The solvent is usually in the MM region, and its electronic effect on the QM region is often described by placing point charges. A lot of effort has been invested in the development of methods with a proper definition of these charges and their placement. The situation for transition metal chemistry has been somehow different, because, while the description of the electronic effects from the MM region may not be that important, the handling of covalent connections between the QM and MM regions is critical. These schemes provide a computationally economical and methodologically robust method to introduce the steric effects of the MM region in the calculation, allowing the straightforward geometry optimization of both minima and transition states. The total cost of the calculation is only slightly larger than the corresponding QM calculation for the QM region. The downside of these methods is that in principle they neglect the electronic effects of the MM region on the QM atoms. Even this limitation can nevertheless be used advantageously to facilitate the analysis of the results [80]. Not surprisingly, the have found the most succesful applications in cases where regioselectivity and enantioselectivity are critical. Among the reactions succesfully studied with the IMOMM and ONIOM methods, one can mention olefin dihydroxylation [82], homogeneous olefin polymerization by early [83] and late [84, 85] transition metal complexes, olefin hydrogenation [86], addition of diethylzinc to aldehydes [87] and hydroformylation [88]. A number of these applications are presented in detail in the remaining chapters of this book, and because of this they will not be discussed here. The QM region is described by including capping hydrogen atoms for the connections with the MM region. The rest of the system, consisting of most of the bulky benzoxantphos ligand, constitutes the MM region. The accurate description of the metal and its attached atoms, and the steric effects of the chelating phosphine are in this way introduced in the calculation, which predicts correctly the experimentally observed regioselectivity leading to the linear product. An interesting additional conclusion of this result is that the electronic effects of the phosphine substituents are not critical for selectivity. The recent application of the methods in the field leaves still some margin for methodological improvement. The application of these methods in homogeneous catalysis should therefore increase in the near future. This is not by accident, because we intended to give the reader an idea of what can currently be done. From its reading, one could however get the wrong impression that everything is already solved from a methodological point of view, and that the only work left is the application of these methods to practical experimental problems. This is certainly not the case. This section collects some of the problems that still remain a challenge for computational chemistry, with special attention to what progress is currently being made. First we will discuss the aspects related to the electronic description of the metal center and its immediate environment. The first problem which must be mentioned in this concern, and that has been already discussed above, is that of non dynamic correlation [38]. Non dynamic correlation appears associated to near degeneracy, that is, the presence of excited electronic state states very close in energy to the ground state. The treatment of this situations is still a challenge for theoretical methods, with the best choice being probably now the computationally demanding HF-based CASPT2 method [44]. The presence of important non dynamic correlation is not a rarity in homogeneous catalysis, and it is usually present whenever a metal-metal bond exists in a polynuclear complex. A second problem in the electronic description of the reaction center is the presence of different spin states in the catalytic cycle, with the system changing between them in what is labeled as spin crossing [89]. In order to properly reproduce the crossing of two states one needs to start from a fairly accurate knowledge on the potential hypersurface of both of them, which in turn requires a good description of excited states, which is by no means easy. Research is currently active in the development of methods which can accomplish a good description of excited states in medium size transition metal complexes, the best current alternatives being

probably CASPT2 [44] and time-dependent DFT TDDFT [90]. After one has a reasonable description of the two surfaces, its crossing must be explored both from the point of view of the distribution of nuclei and of the spin-orbit coupling of the electronic wavefunctions [91]. Spin crossing has not yet an easy solution from a computational point of view, but it has been explored theoretically for some catalytic processes [92, 93]. Apart from the solving of particularly complicated problems, methological development is also involving intense efforts in the direction of improving the performance of the available computational methods. This has an obvious impact in computational chemistry by allowing the study of larger and larger systems. Two particularly fruitful approaches in this Computational Methods for Homogeneous Catalysis 17 concern are the use of pseudospectral methods [94] and of planar waves [95] within the DFT formalism. The proper treatment of the electronic subtleties at the metal center is not the only challenge for computational modeling of homogeneous catalysis. This would be an exact model of reality if reactions were carried out in gas phase and at 0 K. Since this is conspicously not the common case, there is a whole area of improvement consisting in introducing environment and temperature effects. Reaction rates are macroscopic averages of the number of microscopical molecules that pass from the reactant to the product valley in the potential hypersurface. An estimation of this rate can be obtained from the energy of the highest point in the reaction path, the transition state. This approach will however fail when the reaction proceeds without an enthalpic barrier or when there are many low frequency modes. The study of these cases will require the analysis of the trajectory of the molecule on the potential hypersurface. This idea constitutes the basis of molecular dynamics MD [96]. Molecular dynamics were traditionally too computationally demanding for transition metal complexes, but things seem now to be changing with the use of the Car-Parrinello CP method [97]. This approach has in fact been already succesfully applied to the study of the catalyzed polymerization of olefins [98]. Homogeneous catalysis takes place usually in solution, and the nature of the solvent can seriously affect its outcome. There are two main approaches to the introduction of solvent effects in computational chemistry: Continuum models consider the solute inside a cavity within a polarizable continuum. They are quite succesful in capturing the essential qualitative aspects of solvation, but they have the big disavantage of neglecting any specific intermolecular interaction. The most popular continuum model is probably the polarizable continuum model PCM []. Explicit solvent models are formally simpler, because they consist in introducing the solvent molecules together with those of the solute. There are therefore quite a few methodological challenges remaining for the computational modeling of homogeneous catalysis. This must prompt theoreticians to sharpen their tools and interested experimentalists to keep an eye on the development of new methods. Progress is also been made in the development of new methods to tackle reactions where these approaches fail, like those involving spin crossover or those without enthalpic barrier. The tools are thus available for the computational elucidation of the mechanism of catalytic cycles. The only remaining question is whether this mechanistic knowledge is still necessary. Certainly, the highly efficient automation of tests provided by combinatorial chemistry [] allows catalyst optimization without such mechanistic information. We believe however that the detailed knowledge of reaction mechanisms will continue to be, at least in selected cases, a valuable tool for the design of new and more efficient catalysts, and that computational modeling has become an extremely powerful tool to gain this knowledge. Organometallic Bonding and Reactivity. Fundamental Studies, Brown, J. Computational Methods for Homogeneous Catalysis 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 19 Introduction to Computational Chemistry, Jensen F. Computational Organometallic Chemistry, Cundari, T. Advances in Chemical Physics, Rice, S. New York ; Vol. Comprehensive Asymmetric Catalysis, Jacobsen, E. Orbital Interactions in Chemistry, Albright, T. Acta , 31, Modern Quantum Chemistry, Szabo, A. Computational Organometallic Chemistry, T. New York, , page Organometallics , 16, B , 38, B , 37, B , 34, B , 46,

Chapter 2 : Computational Modeling of Homogeneous Catalysis (Catalysis by Metal Complexes) - PDF Fre

Computational Modelling of Homogeneous Catalysis is an extensive collection of recent results on a wide array of catalytic processes. The chapters are, in most cases, authored by the researchers who have performed the calculations.

This result suggests the existence of two bound water molecules at the active site of the mammalian GPx. However, notably, even the RMS deviation of 1. Without excluding other possibilities, this study suggests that the active site of the 2. Peroxidase Activity The catalytic cycle of the peroxidase activity of GPx can be described by the following overall reaction: In II, the H_2O_2 molecule binds to the active site by forming strong hydrogen bonds with the water molecule and the Gly50 residue. This process is found to be exothermic by 6. From the complex II, the reaction is suggested to proceed via a stepwise pathway, which is divided into two parts: As a result, a water molecule and selenenic acid IV are formed. In this part, the proton previously transferred to Gln83 residue moves to the terminal oxygen atom of H_2O_2 and cleaves the OaO bond, forming selenenic acid and a water molecule IV. The barrier for this process is 7. The calculated barrier for the hydrogen peroxide reduction is in excellent agreement with the experimentally measured barrier of Reaction 1 is calculated to be exothermic by In this process, synchronously, the SaH bond of the glutathione is broken and a proton is transferred to the hydroxyl group of the selenenic acid accompanied by the formation of a SeaS bond. Reaction 2 is calculated to be exothermic by We have explored several pathways for this reaction before suggesting the most plausible one. In this step, the SaH bond of the glutathione is broken and the proton is transferred via two water molecules to the amide backbone of Gly The amide backbone of Gly50 directly participates in this process and the presence of two water molecules is essential to bridge the proton donor glutathione and the acceptor Gly50 sites. The calculated barrier for this step is This step is proposed to be a rate-determining step of the entire catalytic mechanism, which is in agreement with experiments Figure 1. Formation of the selenol EaSeH is exothermic by The most relevant results of the previous study are: Our calculations showed that EaSeH is the most preferable active form of the enzyme [25]. In general, selenenic acid [EaSeOH] formation could occur either via a concerted or stepwise mechanism. During optimization both Gln83 and Trp re- 1. In the presence of the protein environment the SeHaO1 bond 1. As shown previously, the stepwise mechanism consists of two steps: In this process the Gln83 residue plays a role of proton acceptor. This proposal concerning the participation of the Gln83 residue in the reaction is consistent with the available experimental information [20]. The computed barrier for the creation of selenolate anion from structure II is However, this value could be slightly overestimated because B3LYP is known to overestimate the activation energy of long-range proton transfer processes [36]. This step is calculated to be endothermic by The absence of the active site water molecule slightly increases both barrier and exothermicity by 1. The calculated barrier for this process is 6. Since this step follows the These results show that the presence of surrounding protein slightly increases the overall barrier by 0. The absence of the water molecule at the active site increases the barrier by 2. This step of the stepwise formation of selenenic acid is calculated to be exothermic by Reductase Activity The suggested mechanism shown in Figure 1. In IIP, peroxynitrite interacts with the active site through hydrogen bonds with water molecule, selenolate and the Gly50 residue. The binding energy of a free peroxynitrite to I0W is calculated to be The computed binding energy of free peroxynitrous acid is only 0. Since the source of the hydroxyl group is not known, both possibilities are explored in this study. It is exothermic by There is no stepwise mechanism corresponding to this step, as the OaO bond cleavage and hydroxyl group transfer are strongly coupled and cannot go through an intermediate. The stepwise mechanism consists of two parts: The overall process IIPA! IIIPA is exothermic by In the absence of a water molecule in the model this barrier is further increased by 5. II 0 PA process is endothermic by 5. The absence of the water molecule in the model increases the barrier by 6. The barrier for this process is only 1. This step of Reaction 1 is calculated to be exothermic by Since the overall barrier for the stepwise mechanism [6. The aforementioned results explicitly indicate that the Gln83 residue plays a key role as proton acceptor step 1 and donor step 2 ,

which is consistent with the available experimental suggestion that the Gln83 residue participates in the catalytic cycle [20]. Moreover, the water molecule located near the Se-center also plays a very important role by directly participating in the reaction and reducing the barriers. Compared with H_2O_2 reduction by GPx, where the calculated barrier for the enzyme oxidation through the identical stepwise mechanism is reported to be Remaining Steps of the Oxidation Pathway In this pathway, subsequent to the formation of selenenic acid [EaSeAOH], the remaining two steps Reactions 2 and 3 follow identical mechanisms, as suggested for H_2O_2 reduction by GPx in 19 20 1 Computational Insights into the Structural Properties and Catalytic Functions of Selenoprotein our previous computational study [25]. Therefore, these two steps are not discussed here. The enzyme may be set-up to control these ions but this unknown regulation process is hard to model. The formation of this intermediate is exothermic by Removal of the water molecule from the model increases the barrier for this process by 7. However, all attempts to locate the transition state for the O1 aO2 bond splitting of O3NO2O1H failed as its optimization always led to the above discussed concerted mechanism. Based on this result it can be concluded that the stepwise mechanism for the formation of the EaSeaOaNbO product does not exist. The barrier for this concerted mechanism is In this process a long-range proton transfer also takes place, which could be slightly overestimated by the B3LYP method [36]. The calculated barriers for the nitration of the selenocysteine by peroxynitrous acid through the isomerization and direct mechanisms, While the direct mechanism is slightly preferred, the accuracy of the methods applied in this study does not allow a clear discrimination. As shown in Figure 1. The barrier for this step is calculated to be 9. Moreover, the direct participation of a water molecule also provides an additional hydrogen bond. Our discussion is divided into four parts. It was found that the inclusion of two water molecules at the active site provides the lowest root mean square RMS deviation from the X-ray structure. Based on these results it was concluded that active site of the enzyme is most likely to have two water molecules. This study reveals important catalytic roles played by Gln83, Gly50 residues and two water molecules. In addition, the generation of the oxidized form of glutathione was proposed to occur with a barrier of The third part explored the role of the protein surroundings in the mechanism of H_2O_2 reduction, using whole monomer atoms in amino acid residues , with ONIOM QM: It was also shown that the rate-determining barriers remain the same, Trends in selenium Chemistry, Nat. References 4 Mills, G.

Chapter 3 : Computational Modeling for Homogeneous and Enzymatic Catalysis - PDF Free Download

Homogeneous catalysis is an area of chemistry where computational modeling can have a substantial impact []. Reaction cycles are usually multistep complicated processes, and difficult to characterize experimentally [].

Download CV here Dr. Jin-Xun Liu received his Ph. His current research interests are focused on theoretical catalysis including structure sensitivity of nanocatalysts, reaction mechanisms, and nanoscale effects in heterogeneous catalysis and electrocatalysis using DFT, molecular simulation, and machine learning. D Candidate Frank Doherty obtained his B. Prior to attending the University of Michigan, Frank worked as an environmental engineering consultant in Maryland and gained onsite experience working at a cement manufacturing facility and a coal-fired power plant. In his free time, Frank enjoys reading, cooking, swimming, and singing. D Candidate Jacques completed his B. His research interests include heterogeneous catalysis, electrochemical surface science, and data science. In his spare time, Jacques enjoys cooking, live music, and the outdoors. He is co-advised between Prof. D Candidate Zixuan obtained her B. Her research interests include heterogeneous and electrochemical catalysis for applications in the nitrogen cycle. Nirala Singh and Prof. In her spare time, she likes to attend yoga and dance classes. Before coming to University of Michigan, Sam served for two years as a logistics and product engineer in Maryland. His research interests include first-principles modelling of energy and environmental catalysis systems, machine learning, and database science. In his free time, Sam enjoys swimming, music composition, and organ performance. D Pre-Candidate Isaiah obtained his B. His research interests include electrocatalysis, energy, and the environment. In his spare time, Isaiah enjoys cooking, exercising, and music. Student Eunbyeol Ko obtained her B. Her research interests involve modeling electrocatalysts for redox flow batteries, machine learning, and data science. In her free time, she enjoys cooking and hiking. He has been part of the Goldsmith lab since June He enjoys reading, running, and playing cards with friends. He is studying 1 heterogeneous catalysis by transition metal single atoms and nanoparticles supported on metal oxides using a genetic algorithm and 2 hydrogenation of bio-oils. He has been part of the Goldsmith Group since December He enjoys playing tennis and reading in his spare time. Jacob is currently studying 1 the impact of temperature and van der Waals interactions on the stability of nanoclusters and 2 vanadium ions in aqeuous redox flow batteries. In the summer of , he did a week research internship with Prof. Two-to-three dimensional transition in neutral gold clusters:

Chapter 4 : Computational Modeling of Homogeneous Catalysis : Feliu Maseras :

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Chapter 5 : Get Computational modeling of homogeneous catalysis PDF - Advanced Imaging Library

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Chapter 6 : Catalysis - Software for Chemistry & Materials Software for Chemistry & Materials

Enantioselective Hydrosilylation by Chiral Pd Based Homogeneous Catalysts with First-Principles and Combined QM/MM Molecular Dynamics Simulations Alessandra Magistrato, Antonio Togni, Ursula RÃ¶thlisberger, Tom K. Woo.