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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（理学）　氏名　趙　黎明

学 位 論 文 題 名

Theoretical Study on the Mechanism of Transition Metal Catalyzed Reactions and Spin-Forbidden Reactions
（遷移金属錯体による触媒反応およびスピン禁制反応のメカニズムに関する理論的研究）

Transition metal catalysts are one of the most important homogeneous catalysts. They have been applied to many fundamental chemical reactions. The Wilkinson complex is one of the famous transition metal catalysts. This Rh containing catalyst promotes hydrosilylation and has been studied for many years. However, mechanistic discussions were limited to existing three classical mechanisms, Chalk-Harrod (CH), modified Chalk-Harrod (mCH), and outer-sphere mechanisms. In this study we investigated different mechanisms, especially, two new mechanisms, alternative Chalk-Harrod mechanism (aCH) and double hydride (DH) mechanism which were never considered before. On the other hand, because of active d orbital electrons, the spin-forbidden processes are involved in many reactions catalyzed by transition metal complexes, although they were thought to be difficult to take place. There are some conflicting experimental observations for spin-forbidden reactions, some of them were fast while some are not. The debates whether spin crossing would slow the reactions are reconciled in computational chemistry. The minimum energy intersystem crossing points (MEISCPs) are the key points to reveal the mechanism of the reaction. With curiosity about spin crossing reactions, two special cases were investigated. One is the the spin crossing in biochemical reaction which can be found in Chapter 3. Another simple case is the photo-induced organic reaction as explained in Chapter 4. The experience of locating MEISCP in these examples led us to the direction of method development. We successfully applied penalty function method to the nudged elastic band (NEB) method to automatically search MEISCP and transition states (TS) simultaneously.

In Chapter 2, a systematic research about homogenous Rh catalyst in hydrosilylation reaction with ketone and alkene was explained. Previously proposed three mechanisms, Chalk-Harrod (CH) mechanism, modified Chalk-Harrod (mCH) mechanism, as well as outer-sphere mechanism were examined. Besides, we also found two mechanisms, aCH mechanism and DH mechanism. Different from the expectation that acetone hydrosilylation should take place through mCH mechanism, we found the CH mechanism is much more preferred. Our newly proposed aCH mechanism where the active species is a four coordinated complex was found to have similar energy barrier as the CH mechanism. As we know, CH mechanism is widely applied in many other reactions. Considering the similar performance of CH and aCH mechanism, we suggest to estimate the aCH mechanism if the CH mechanism is found to be applicable. Moreover, the lowest energy barrier of acetone and ethylene hydrosilylation appeared in the newly proposed DH mechanism. The active species of DH mechanism is a six coordinated Rh complex with two Rh-H bonds. We found that the

extra Rh-H bond can effectively improve the catalyst's performance. Thus, we suggest to consider strategies to directly synthesize or to generate in situ such a catalyst with double Rh-H bond catalyst to improve the reactivity.

In Chapter 3, a theoretical study of myoglobin catalyzed cyclopropanation was investigated with two models. In the experiment, iron porphycene substituted myoglobin (rMb) was found to be much more active than the wild-type myoglobin (nMb) in the styrene cyclopropanation with ethyl diazoacetate. With heme complexes (Fe-porphyrin-imidazole and Fe-porphycene-imidazole) model, the DFT results explained the reactivity difference by the different number of MEISCPs, the position of the MEISCPs, and the different total activation energy. These results indicate that for spin-forbidden reactions it is necessary to optimize the structure of MEISCPs. A larger model, which includes both protein environment and some solvent water molecules, was employed for further research. The calculated potential energy surfaces are similar to that of small model. Thus, the basic conclusions remain same. However, the relative potential energy of some intermediates is changed. The reasons for the changes can be attributed to two aspects. First, the protein environment can change the electronic structure of the active site. Second, the solvent water was found to influence the complex stability through hydrogen-bonding. Finally, we first applied free energy perturbation (FEP) method to the heme system to calculate the free energy surfaces. The simulation results of the MEISCPs indicated that the energy of the crossing point is majorly determined by the QM part. In other words, if the QM structure is optimized to the MEISCP, most of the trajectories from the simulation with this frozen QM structure are on the crossing seam. This first attempt to apply FEP method together with ONIOM method shows the possibility to evaluate the influence of the fluctuation of the protein and the solvent in an explicit way for such myoglobin system. It's worthy to mention that if enough computational resource is available, the solvent should be carefully considered not only in the simulation, but also in the single point energy evaluation.

In Chapter 4, a method to locate MEISCP in multiple spin states reaction was developed. This new method explores the reaction pathway, like intrinsic reaction coordinate (IRC) method, but conducted on the multiple electronic surfaces. In a case study, a penalty function method was applied to locate MEISCP in a newly reported reaction, photo-induced β-elimination of 9-fluorenylmethanol leading to dibenzofulvene. The process of using theoretical tool to study spin crossing reaction was displayed. The experience of the case studies provided a direction of our method development. Basing on the merits of traditional nudged elastic band method and the penalty function method, we proposed a new approach to combine these two methods and accomplished by Fortran coding. Through this new approach, it is possible to locate MEISCP and TS while optimizing the reaction path. The program was tested in three cases ethylene rotation, In_2 catalyzed C-H bond activation, and the CoH^+ catalyzed C-H bond activation. The definition of the candidate for the MEISCP was found significantly important. In the simple cases where only one MEISCP is on the reaction pathway, a so-called two-image selection scheme is enough. However, for more complicated case where intersystem crossing happens more than once, like CoH^+ catalyzed C-H bond activation, we defined a three-image selection scheme to reduce the number of special points. In all of the three systems, calculated reaction pathways are converged near to minimum energy pathways. Besides, we also proposed a revised version of multiple states nudged elastic band method to improve the precision of the calculation.