Abstract

論 文 の 内 容 の 要 旨

論文題目　Theoretical studies on the reaction path of hydrogen transfer with many-body effects

（水素移動反応の多体効果を考慮した反応経路に関する理論的研究）

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Introduction

Proton transfer (PT) and hydrogen transfer (HT) reactions are fundamental and important for various processes in chemistry and biology. The mechanisms of these reactions have mainly three important features; quantum tunneling of the proton, solvent control of the reaction coordinate, and strong couplings of skeletal vibration with reaction coordinate. In some cases of the strong couplings of skeletal vibration, the reaction path is not introduced by geometric information of potential energy surface. Then these reactions are often investigated by ab initio molecular dynamics and the reaction mechanisms are described as the feature of geometry in each system. In this study, I investigate the effect of the change of the electronic structure in molecular skeleton on hydrogen transfer mechanisms by valence bond theory. Furthermore I analyze the fundamental process of dehydrogenation of ammonia borane.

Proton transfer in protonated benzene

As is shown in the example of anharmonic couplings of the proton to many degrees of freedom of the molecules, I focused on protonated benzene ($C_6H_7^+$)[1], given in Figure 1. In terms of valence bond theory, the carbon with two proton atoms makes sp^3 hybrid orbital and the others form sp^2 hybrid orbital. In order to examine the coupling between proton transfer and the hybridization of carbon atoms, all the degrees of freedom must be treated equally. Therefore ab initio molecular dynamics simulation is performed to examine the mechanism of proton transfer reaction in the protonated benzene. The potential derivatives have been calculated with the MP2 method of the 6-31G(d, p) basis set in the GAMESS package. The Gear predictor-corrector method is used to integrate the equations of motion for nuclear with an integration time step of 0.2 fs. The total energy is set to 3.765 eV, which is higher than the zero-point vibration energy of the system. 284 trajectories were obtained and the ensemble of sampled trajectories has totally 700 proton transfers. Relative coordinates were introduced in order to identify the geometry in trajectories. Suppose the hydrogen atom H(*i*) locates between carbon

(a)　(b)

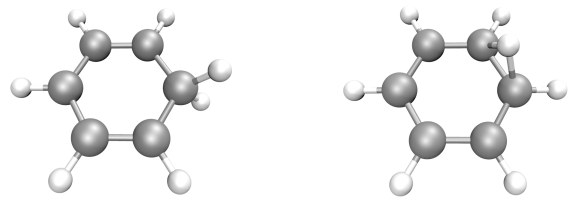


Figure 1: Stable structure (a) and transition state structure in intramolecular proton transfer (b) of protonated benzene

atoms C(j) and C(j+1). The center of gravity of the six membered ring is set to G. The vector GH'(i) is defined as a projection of GH(i) vector on the plane containing three points, G, C(j), and C(j+1). The relative coordinate α, parallel to reaction coordinate is defined

$$\alpha(i) = \frac{\angle \mathrm{C}(j)\mathrm{GH'}(i)}{\angle \mathrm{C}(j)\mathrm{GC}(j+1)}, \qquad (1)$$

and the perpendicular coordinate β is represented as

$$\beta(i) = \angle \mathrm{H}(i)\mathrm{GH'}(i) \ . \qquad (2)$$

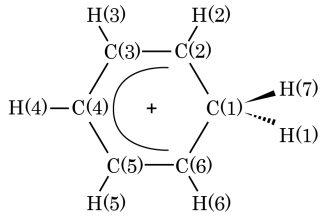


Figure 2: Labels of the atoms

The statistical distribution of $\beta(i)$ for all hydrogen atoms (i = 1, …, 7) only at the moment of proton transfers is shown in Figure 3. The sharp peak around β = 0 corresponds with the hydrogen atoms locate almost on the six membered ring and two small peaks of around β = ±40 corresponds to the transition state structure for transferred proton. In other words, the peak around β = 0 is assigned to sp^2 hybrid orbital. Therefore I approximately fit the peak of $\beta \approx 0$ by a normal distribution with mean μ = -1.25 and standard deviation σ^2 = 19.39. The normal distribution is shown with the solid line in Figure 3. I define that the carbon atom forms sp^2 hybrid orbital by the following condition,

$$\mu - 2\sigma \leq \beta \leq \mu + 2\sigma \ . \qquad (3)$$

By using the electron structure definition given in Equation (3), the statistical distribution of $\alpha(i)$ for transferred proton can be divided into 4 types of combinations of hybridization of two carbon atoms, (sp^3, sp^3), (sp^3, sp^2), (sp^2, sp^2) and (sp^2, sp^3) shown in Figure 4(a)-(d). The case of (b), corresponding to the (sp^2, sp^2) combination represented by the transition state, has much components around α = 0. It indicates that both sides of the carbon atoms form sp^2 hybrid orbitals and the proton could attach to the neither the carbon atoms near the proton, the transferred proton is trapped and vibrates around the transition state. For the sp^2 hybridizations, transferred proton has bounded potential at the center of two carbon atoms, and could not attach to any carbon atoms.

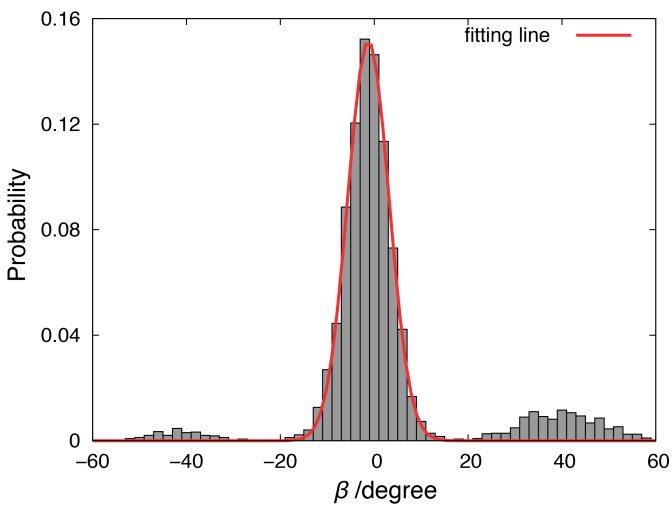


Figure 3: Histogram of β with the fitting line by standard distribution.

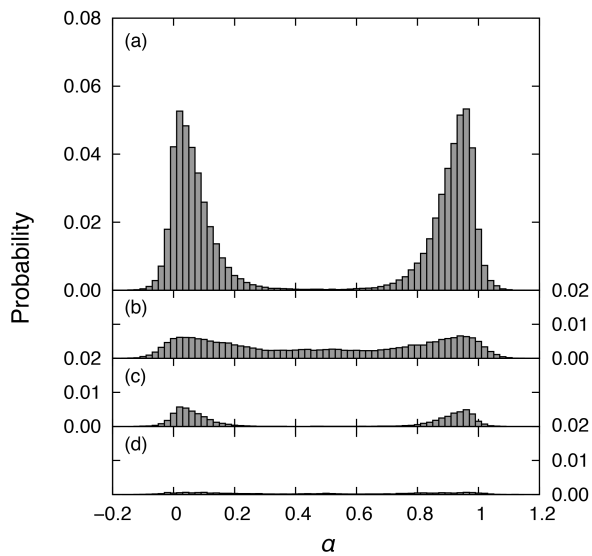


Figure 4: Histogram for relative coordinate α from transferred proton in all trajectories, divided into (a)(sp^3, sp^2), (b)(sp^2, sp^2), (c)(sp^3, sp^3), and (d)(sp^2, sp^3) by Equation (3).

Transition metal catalyzed dehydrogenation of ammonia borane

Ammonia borane (AB $=NH_3BH_3$) has been studied as a chemical hydrogen-storage material because of the high gravimetric capacity of hydrogen in AB (19.6 wt %). Although releasing H_2 from AB takes place thermally without a catalyst, high temperatures and slow reaction rates are the main drawbacks to use of AB as a carrier for dehydrogen. In contrast, metal-catalyzed release of H_2 from AB could operate at a lower temperature and produce H_2 at a much faster rate[2].

In recent study by Bhattacharya et al, a series of iron bis(phosphinite) pincer complexes (shown in Figure 5) are found to catalyze dehydrogenation of AB[3]. They can afford to release 2.3-2.5 equiv of H_2 per AB in 24h. Among them, (c) exhibits the highest activity, followed in order by (b) and (a). The proposed catalytic cycle is shown in Scheme 1. The rate-determining step involves breaking the N-H and B-H bonds of AB, which results in the protonation of *ipso* carbon and the transfer of a hydride ligand from boron to iron. In this study, I verify the proposed reaction cycle and determine the cause of the difference of the catalytic activity by examining the influences of ligands.

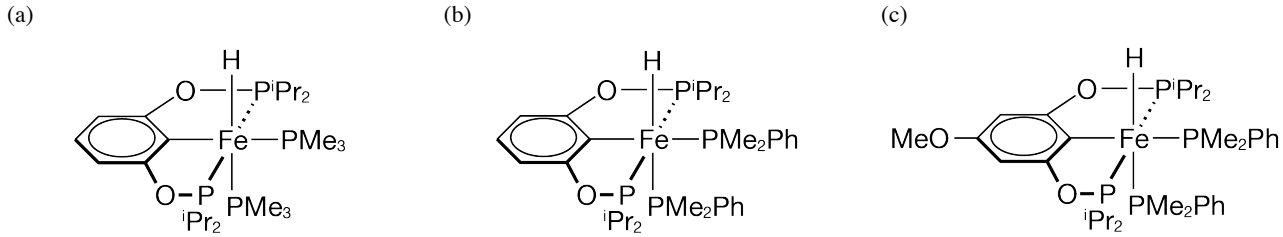
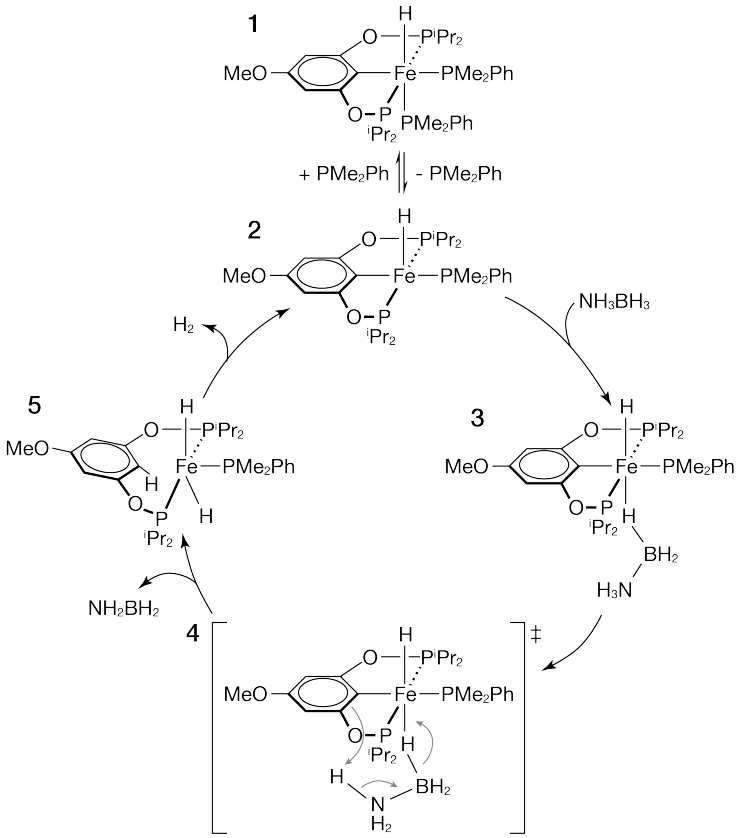


Figure 5: Iron POCOP-pincer complexes. I calculated them that isopropyl groups replaced to methyl groups, and refer to replaced (a)- (c) as compound A, B and C, respectively.

Scheme 1: Catalytic cycle for the dehydrogenation of AB catalyzed by Figure 5(c), proposed by ref[3]



By the energy diagram calculation, it was revealed that the rate-determining step in A is hydride and proton transfer, while that in B and C is the release process of the PMe_3 or PMe_2Ph substituent opposite to hydride. The catalytic activity was correspond to the experimental results. The rotation PMe_3 and PMe_2Ph groups in 2, 3 and 5 largely effects on their potential energy. By addition of AB to 2, PMe_3 or PMe_2Ph group is rotated. Due to the rotation, the B-N bonding would be shorter and it stabilizes the compound. At the same moment, NH_2BH_2 is liable to eliminate. It is equal to hydride and proton transport to the catalyst. In this way, the intermediates and transition states of B and C in hydride and proton transfer reaction is stabilized and the activation barriers would be lower. Moreover, the methoxy group on aromatic ring is electron-donating group because of the resonance interactions of the lone pairs of the oxygen atom with the antibonding π^* orbitals of the aromatic ring. The interactions by the methoxy group more stabilize the each compound of C, including C-2 which forms the highest potential barrier.

Discussion and conclusions

In the study of proton transfer in protonated benzene, I detected the geometry of the hydrogen, not transferred proton, as the feature of the molecular structure in PT processes. On valence bond theory, the feature can be converted into hybridized orbital. Then I elucidated that the reaction path is controlled by the transformation between sp^3 and sp^2 hybridization of carbon atoms and sp^2 hybrid orbital does not allow the proton to make a bond with carbon.

On the other hand, nitrogen-boron bonding was extracted as the feature of molecular structure in AB dehydrogenation catalyzed by the Fe POCOP-pincer complexes. This system is never the same with protonated benzene as atomic species, but just the same as electron structure. The isoelectronic AB and CH_3CH_3 elucidated that the key step of hydride and proton transport with released NH_2BH_2 in the dehydrogenation is to form sp^2 orbital on nitrogen and boron. Then the reaction mechanism is described by using the dynamical electronic information of protonated benzene. Moreover the interpretation is useful to reveal the role of ligands of dehydrogenation catalysts.

Examine of proton transfer reactions considering the many-body effects make clear the behavior of the number of degrees of freedom around them. It also leads to design the hydrogen transfer reaction paths including catalytic dehydrogenation.

References

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