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Theoretical study of the chemical reactions by the combination of quantum mechanical and molecular dynamics methods**Toshiaki Matsubara**

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I will introduce two subjects^{1,2} we have examined by the combination of quantum mechanical and molecular dynamics methods I. It has been known that the nucleophilic substitution at the Si atom, $\text{SiH}_3\text{Cl} + \text{Cl}^- \rightarrow \text{SiH}_3\text{Cl}^* + \text{Cl}^-$, proceeds by two steps with the inversion or retention of the configuration passing through an intermediate with the trigonal bipyramid (TBP) structure (Figure 1), although the conventional $\text{S}_{\text{N}}2$ reaction at the C atom proceeds by one step with the inversion of the configuration passing through a transition state with the TBP structure. We followed by the QM method all the possible paths and found that TBPcis produced with a high probability is readily transformed to the energetically more stable TBPtrans. In order to obtain more information concerning the trajectory of Cl^- on the dissociation from TBPtrans, which we cannot clarify on the basis of the energy profile determined by the QM method, we conducted the MD simulations with and without the water solvent. The QM-MD³ simulations without the water solvent revealed that the dissociation of Cl^- from TBPtrans occurs without passing through TBPcis. The ONIOM-MD³ simulations with the water solvent further suggested that the thermal fluctuation of the water solvent significantly affects the oscillation of the kinetic and potential energies of the substrate to facilitate the isomerization of the TBP intermediate from the cis form to the trans form and the subsequent dissociation of Cl^- from TBPtrans. II. Germanone $\text{R}_2\text{Ge}=\text{O}$ have not been isolated until recently, because it easily oligomerizes due to its instability. However, Tamao et al. recently succeeded to isolate the germanone (Eind)₂Ge=O by the incorporation of bulky substituents called Eind. The isolated (Eind)₂Ge=O is very reactive and the reactions that do not proceed in the case of ketone easily proceed in the case of germanone. For example, the σ bond of water adds to the Ge=O of germanone to form the germanediol at room temperature. In this study, we examine the mechanism of the σ bond cleavage of the substrate on the Ge=O bond. In the case of H_2O , the QM calculations showed that the H_2O coordinates to the Ge before the σ bond cleavage (Figure 2) and this coordination induces a heterolytic σ bond cleavage. We further performed the QM-MD³ simulations and found that the kinetic energy concentrates on the coordinated H_2O oxygen to strongly oscillate the coordinate bond. This oscillation further enlarges just before the O-H σ bond cleavage. The kinetic energy of this oscillation would be transmitted to the normal mode of the O-H bond breaking. Thus, the coordination and the vibration of the H_2O oxygen was thought to be an important driving force of the O-H σ bond cleavage.



Figure 1. Possible nucleophilic substitution at the Si. The relative energies (kcal/mol) at the B3LYP level are also presented together.

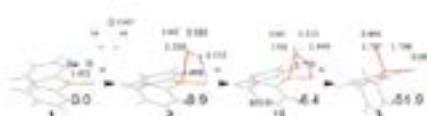


Figure 2. Optimized equilibrium and transition state structures (Å) of $\text{Ph}_2\text{Ge}=\text{O} + \text{H}_2\text{O}$ at the B3LYP level. The relative energies (kcal/mol) are also presented together.

Biography

Toshiaki Matsubara is working as a Professor in Department of Chemistry, Faculty of Science, at Kanagawa University, Japan.

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