1. Introduction

Chemical reaction analyses are usually based on the reaction energy diagrams of the optimum energy paths without respect to the electronic structures of molecules. In particular, the reactivities of gas-phase reactions are usually discussed only using the reaction barrier heights. The frontier orbital theory is an exceptional method to investigate the gas-phase reactivities by explicitly considering molecular electronic structures [1]. In this method, the reactivities are discussed by illustrating the diagram of valence orbital images and their orbital energies. Note, however, that reaction analyses based on this diagram have been carried out using only the orbital phase images. That is, orbital energies are taken only as a guide, because there has been no method to give orbital energies quantitatively.

Currently, there is one theory that can reproduce orbital energies quantitatively: long-range corrected (LC) density functional theory (DFT) [2]. Long-range correction complements long-range exchange interactions, which are usually neglected in DFT, into exchange functionals by combining the long-range part of the Hartree-Fock exchange integral. Despite of its simplicity, the long-range correction comprehensively solves conventional DFT problems in the calculations of, e.g., van der Waals bonds, charge transfer excitations, and optical properties including hyperpolarizabilities [3]. It was recently revealed that the Kohn-Sham (KS) method using LC functionals quantitatively reproduce both occupied and unoccupied valence orbital energies [4], which correspond to the minus ionization potentials and electron affinities, respectively [3], for the first time ever. The accurate LC-KS orbital energies make it possible to carry out the reaction analyses based on orbital energies.

We recently obtained an interesting result for the relation between chemical reactions and orbital energies [5]. Plotting the HOMO-LUMO gaps of the LC-KS method on the intrinsic reaction coordinates (IRCs) of Diels-Alder reactions showed that the gaps are kept almost constant in the initial reaction processes and rapidly increase around the transition state structures. It is proven that the orbital energy gradients on IRCs come from geometric transformations and charge transfers and that charge transfers do not vary fractionally-occupied orbital energies. The constant HOMO-LUMO gap gradients in the initial reaction processes, therefore, indicate that the reactions initially proceed with charge transfer, while geometric transformations being negligible.

In this study, we propose a new method for evaluating reactivities based on the orbital energy gaps between the contributing orbitals on the IRCs [6].

2. Method

In the new method, reactions are analyzed as follows [6]:

(1) First, determine the IRC of a reaction by the LC-KS method and then plot the calculated
valence orbital energies on the IRC.

(2) Next, specify the pair of the target orbitals, which mainly donate or accept electrons in the reaction, using the plot of the valence orbital energies on the IRC given above.

(3) Illustrate a reaction diagram plotting the orbital energy gaps of the target orbitals on the IRC.

(4) Finally, calculate the gradient of the normalized orbital energy gap at the reactant structure. The reactions giving small orbital energy gap gradients (OEGGs) less than 0.25 are taken to proceed through the initial charge transfer.

3. Results and discussions

Analyzing the normalized reaction diagrams of 43 fundamental reactions showed that more than 60% of the forward reactions initially proceed only with charge transfers, though only less than 40% of the backward reactions do so [6]. In the reference reactions, there are several anti-activation-energy (AAE) reactions, in which higher barrier heights are given for the forward reactions. Comparing the OEGGs of the AAE reactions indicated that no backward reactions proceed with charge transfers except for the \( \text{CH}_4 + \text{Cl} \rightarrow \text{CH}_3 + \text{HCl} \) reaction. For this exceptional reaction, we found a collision reaction study suggesting that this reaction proceeds a different reaction path than the optimum energy pathway [7]. There are 3 types of the reactions which do not proceed with charge transfers: \( \text{S}_\text{n}2 \), symmetric, and methyl radical reactions. For the \( \text{S}_\text{n}2 \) reactions, Hase and coworkers have questioned the optimum pathways experimentally and have recently proposed that the optimum energy pathways are avoided [8]. Based on the time-resolved ion-molecule crossed beam imaging spectroscopy, they showed that the \( \text{Cl}^- + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{Cl} + \text{I}^- \) reaction takes the roundabout path, in which the \( \text{CH}_3 \) group of \( \text{CH}_3\text{I} \) spins around \( \text{I}^- \) to move to \( \text{Cl}^- \). We suppose that symmetric reactions, in which the reactants are the same as the products, also proceed like the \( \text{S}_\text{n}2 \) reactions because the optimum pathways are analogous to the \( \text{S}_\text{n}2 \) ones. Furthermore, the forward processes of the methyl radical reactions have much higher reaction barriers than the backward ones except for the \( \text{CH}_4 + \text{Cl} \rightarrow \text{CH}_3 + \text{HCl} \) reaction.

References