

# Reaction Energetics of the Diels-Alder Reactions: A Long-range Corrected Density Functional Theory Study

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Diels-Alder reactions have been important targets especially in chemical reactivity calculations. We present the possibility of quantitative reaction analysis on the long-range corrected density functional theory (LC-DFT) [1]. In this study, we first found that the long-range correction for exchange functionals is principally required to quantitatively reproduce the Diels-Alder reaction enthalpies, which have been poorly given by conventional DFTs. Next, It was noticed that the LC-DFTs somewhat overestimate the barrier height energies. However, these overestimations are drastically improved by taking dispersion forces into account by the local response dispersion (LRD) method. We therefore proposed that the dispersion correction is also needed to investigate the overall Diels-Alder reaction processes. Based on the remarkable accuracies of the LC-DFT in the calculations of the Diels-Alder reactions and orbital energies, the behaviors of the global hardness response (GHR), the halves of the HOMO-LUMO gaps, along the intrinsic reaction coordinates were examined. Consequently, we found that the LC-DFTs give suggestive GHR behaviors: GHR is almost constant for the initial processes and then rapidly increases for the subsequent processes. This suggests that orbital energies play a significant role in chemical reactions.

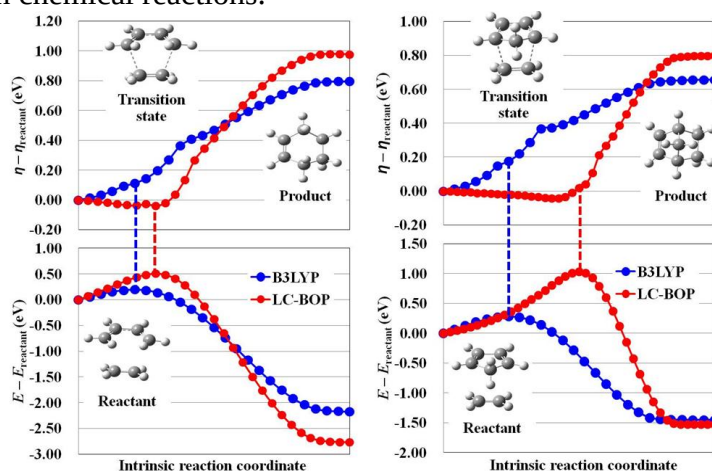


Figure 1: Global hardness responses  $\eta$  and total energies  $E$  along the intrinsic reaction coordinates for the reactions of both butadiene and cyclopentadiene with ethylene.

[1] Singh, R.K., Tsuneda, T. *J. Comput. Chem.* 34 (5):379–386, 2013.