The Role of Dispersion in Catalysis

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Introduction

London dispersion (LD) interactions constitute the attractive part of the van-der-Waals potential and they have been found to provide decisive stabilization in sterically bulky molecules and to enhance catalytic reactivity.[1][2] However, there is no systematic study on identifying effective dispersion energy donors (DEDs).[3]

We carried out a systematic study on quantifying LD interactions by correlating LD interactions energies with the size and polarizability of DEDs. These can be further applied to catalyzed chemical reactions as LD helps understand the contribution of DEDs in the reactivity and selectivity of chemical reactions. Herein, the selectivity of Corey-Bakshi-Shibata Reduction (CBS Reduction) has been reevaluated by accounting the dispersion corrections.[4]

Methods

Conformational research was employed by GFN2-xtb. The reaction energy was computed with and without dispersion correction(D3BJ) by DFT methods at B3LYP/6-311G(d,p). Single point calculations were carried out at M06-L and DLPNO-CCSD(T) level of theory. Solvent effect was also included by SMD model (in THF) in the CBS reduction.

Results

Dispersion energies were found to increase as the size of the molecules. A good linear relationship between dispersion interaction and polarizability per volume (α/V, α: polarizability; V: volume) was established in alkane dimer and benzene derivative dimer. In the hetero alkane dimer, a size match concept was introduced to present the correlation between dispersion energy and α/V.

Based on the theory, it was found the enantioselectivity of CBS reduction was determine by the dispersion interactions between phenyl groups from catalyst and substrate rather than the well-accepted steric repulsion.

Outlook

The important role of attractive dispersion interactions on the enantioselectivity of CBS reduction allows us to explore the challenging cases e.g., alkyl-akyl ketones by tuning the dispersion interactions. With these new insights, we are capable of design new catalyst for the CBS reduction.

Reference

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