Hessisches Kompetenzzentrum
für Hochleistungsrechnen

Functionalization of Hydrocarbons Trough Novel HAT-Agents

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Project Areas
Molecular Chemistry

Software
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Additional Software
Avogadro, Chemcraft

Institute
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Introduction

Alkanes are attractive feedstock chemicals due to their natural occurrence and they offer access to a wide variety of substrates by C–H functionalization. This can be achieved by highly reactive species like carbenes, radicals, carbocations etc. However, selective functionalizations are still rather challenging. On the basis of several heterocyclic compounds (2(3H)-thiazolone, 2(3H)-thiazolthione, 2-imidazolone, 2-imidazolthione) we want to generate highly reactive radical cations, which subsequently undergo selective HAT from unactivated C(sp^3)–H-bonds of hydrocarbons to generate carbon centered radicals. These radicals will afterwards be trapped by electrophilic group transfer agents (tosylcyanide, tosylazide, etc.) to form functionalized hydrocarbons.

Methods

We are using Gaussian16 for modeling organic compounds, compare their ground state energy and calculate binding dissociation energies (BDE) through a homodesmotic equation set. For our needs to compare experimental data with theory we need to compute our structures on a high level of theory. As basis for geometry optimization and energy calculation serve Double-Hybrid-Methods such as B2PLYP/6-311G(d,p). In each of our investigated systems it is very important to know BDEs in order to find suitable systems which exhibit BDEs higher then 100 kcal/mol to facilitate HAT from unactivated C(sp^3)–H-bonds.

Results

In the first period we were able to compute small closed- and open-shell structures to understand the influence of their substitution pattern on their stability, electrophilicity and BDE. Ongoing investigations are about the dynamics of HAT on the basis of a curve crossing model and the development of new systems to achieve selective HAT.

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