

Rupturing Materials in Electric Fields

Quantum Chemical Coupling of Mechanochemistry with Strong Electric Fields

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In Short

- Computational Chemistry
- Density Functional Theory
- Mechanochemistry
- Electric Fields
- Mechanochromic Materials

In mechanochemistry, forces are used to initiate chemical reactions [1]. This approach can be used in the production of mechanochromic materials, which change their color when a threshold stretching force is applied. In the case of a polymer, for example, a molecular subunit, the so-called mechanophore, is embedded in the polymer backbone. Upon application of stretching forces, the mechanophore changes its structure, e.g. *via* bond-rupture or cis/trans-isomerization, which can be accompanied by color changes. The applications of this approach are immense, including optical strain detection in the construction industry, tamper-proof packaging, and self-healing materials.

Oriented external electric fields (OEEFs) have been used to catalyze a number of reactions by lowering the energy of a transition state if a zwitterionic resonance structure, which is favored in an OEEF, is present in the transition state (cf. Figure 1) [2-4]. Examples of reactions induced by OEEFs include enzymatic processes, isomerizations and Diels-Alder reactions. Moreover, it has been demonstrated that OEEFs reduce the bond dissociation energy of σ - and π -bonds and allow the switching of typically homolytic to heterolytic bond rupture processes.

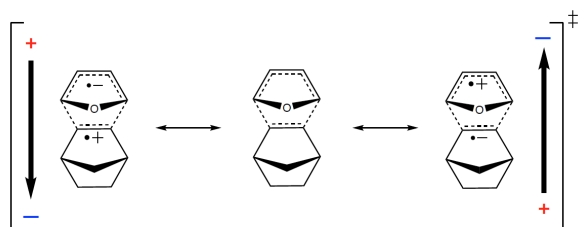


Figure 1: Schematic representation of the resonance structures in the transition state of a Diels-Alder reaction, which can be energetically favored in an oriented external electric field (OEEF).

In this project, mechanochemistry is coupled to the application of OEEFs in order to reduce the rupture forces of mechanophores in mechanochromic materials. While it is far from straightforward to conduct mechanochemical experiments in OEEFs due to the difficulty of controlling the relative orientation of the substrate and the electric field, computational chemistry offers the opportunity to rapidly screen a variety of mechanochemical reactions in OEEFs. The focus in this project lies on determining the rupture forces required to achieve the color switching process, using state-of-the-art computational methods.

One focal point of the first two phases of the project was a thorough benchmark of electronic structure methods that allow an accurate reproduction of energies and geometries of different molecules in OEEFs of various strengths. Reference data was provided by gold standard CCSD[T] calculations extrapolated to the complete basis set limit. Several wavefunction-based quantum chemical methods and a large number of density functionals were tested. It was found that, surprisingly, the accuracy with which a given density functional reproduces CCSD[T] energies and geometries in OEEFs of various strength does not correlate with the rung of this functional on Jacob's ladder (Figure 2). In other words, newer, more sophisticated and computationally more demanding density functionals do not necessarily deliver more reliable results than more traditional functionals. The computationally inexpensive method ω B97X-V/cc-pVDZ, for example, is a suitable choice for molecules in OEEFs. This finding is important for scientists working in various branches of chemistry in which electric fields are present, and not only in mechano-electrochemistry. Our findings have recently been published on a preprint server [5].

Shortly before the end of the first phase of this project, a proof-of-principle study on the behavior of a mechanophore in an OEEF was initiated. It was found that, in agreement with our hypothesis, the rupture force of a model mechanophore can be reduced significantly if an OEEF is present (Figure 3). While this observation has important implications for the design of mechanophores, it was only the starting point for further investigations carried out in the second phase of the project. The calculations conducted in the second project phase allowed an in-depth analysis of the mechanical properties of several commonly used mechanophores. Crucially, the influence of the strength and direction of the OEEF

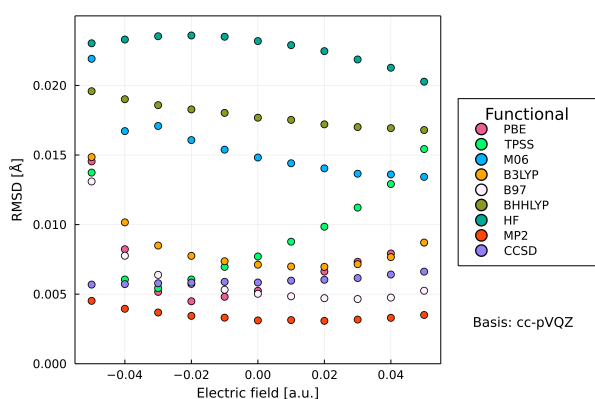


Figure 2: Benchmark of electronic structure methods for the deviation of bond lengths in a test set of 20 organic and inorganic molecules in external electric fields, calculated with various density functionals. Reference data is provided by CCSD[T]/cc-pVQZ.

on the mechanical properties of the mechanophores was investigated in great detail. A publication reporting the full set of calculations will be published shortly. Our findings will allow us to tune the rupture forces in mechanochemical reactions based on a rational design of the mechanophore and its surrounding.

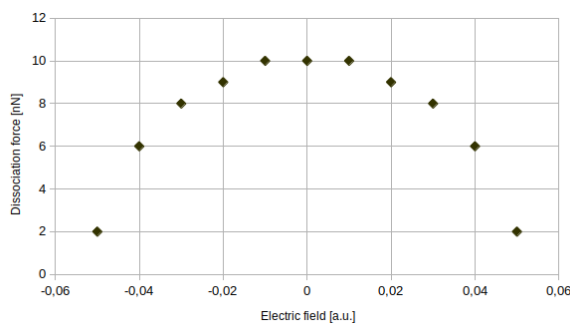


Figure 3: Rupture forces of a model mechanophore in OEEFs of various strengths, calculated with the quantum chemical EFEI method to apply mechanical forces.

Turning to applications, various known (mechano)chemical transformations will be scrutinized as to their applicability in OEEFs, with the aim of increasing the mechanical yield of these processes. This will pave the way for a more widespread use of mechano-electrochemical methods in organic synthesis and materials science.

All mechanochemical transformations in OEEFs are understood in terms of the strain generated by the combined application of mechanical forces and OEEFs, by using the previously developed Judgement of Energy Distribution (JEDI) analysis [6]. This will allow an in-depth analysis of the molecular basis for mechanochemical bond rupture in OEEFs and the subsequent optimization of this process by specifically targeting those bonds that are most susceptible to stretching forces in a given setup.

For the major part of the calculations conducted in the course of this project the Q-Chem program package is used, since it includes a wide variety of density functionals, the External Force is Explicitly Included (EFEI) method for geometry optimizations under external forces, the straightforward application of electric fields and an interface to the JEDI analysis, which allows the determination of the force-bearing scaffold of a mechanically deformed molecule and the subsequent optimization of the mechanochemical response.

In the third phase of the project, its scope will be expanded to the behavior of mechanophores in complex polymer environments. Based on our previous calculations, we will run Molecular Dynamics (MD) simulations on these complex systems and test the simultaneous application of strain and OEEFs. This approach allows the investigation of the mechanical response of realistic functional polymers, paving the way for experimental realization.

In summary, the combination of strong electric fields and mechanochemistry offers the possibility of tuning the rupture forces and consequently the color response of mechanochromic materials with unprecedented precision. State-of-the-art computational methods are applied to model both effects simultaneously, thus preparing experimental verification efforts.

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More Information

- [1] T. Stauch, A. Dreuw, *Chem. Rev.* **116**, 14137 (2016).
- [2] S. Shaik, R. Ramanan, D. Danovich, D. Mandal, *Chem. Soc. Rev.* **47**, 5125 (2018).
- [3] S. Shaik, D. Mandal, R. Ramanan, *Nat. Chem.* **8**, 1091 (2016).
- [4] A. C. Aragonés, N. L. Haworth, N. Darwish, S. Ciampi, N. J. Bloomfield, G. G. Wallace, I. Diez-Perez, M. L. Coote, *Nature* **531**, 88 (2016).
- [5] T. Scheele, T. Neudecker, *ChemRxiv* **2022**, DOI: 10.26434/chemrxiv-2022-db090.
- [6] T. Stauch, A. Dreuw, *Acc. Chem. Res.* **50**, 1041 (2017).

DFG Subject Area

327-01 Theoretical Chemistry: Electron Structure, Dynamics, Simulation