

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. This approach can be used in the production of mechanochromic materials, which change their color when a threshold stretching force is applied. In case of a polymer, for example, a molecular subunit, the so-called mechanophore, is embedded in the polymer backbone. This 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 and temper-proof packaging.

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). Examples of reactions induced by OEEFs include enzymatic processes, isomerizations and Diels-Alder reactions. Moreover, it has been demonstrated that OEEFs decrease the bond dissociation energy of σ - and π -bonds and allow the switching of typically homolytic to heterolytic bond rupture processes.

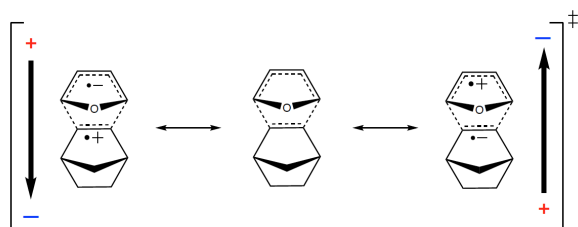


Figure 1: Schematic representation of the resonance structures in the transition state of a Diels-Alder reaction, which can be energetically favored in an oriented external electric field (OEEF).

In this project, mechanochemistry will be coupled to the application of OEEFs in order to achieve decreased rupture forces of mechanophores in mechanochromic materials. While it is far from straightforward to conduct mechanochemical experiments in OEEFs due to the extreme 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. Here the focus lies on determining the rupture forces required to achieve the color switching process, using state-of-the-art computational methods.

The first phase of the project focuses on the determination of the factors that govern the activation of mechanophores in well-known mechanochemical reactions without external electric fields. In particular, the roles of the relative orientation of the mechanophore and the external force, the chemical composition of the mechanophore itself and the linkers to the polymers as well as local topological factors shall be considered and their influence on the rupture forces shall be determined. This will allow us to tune the rupture forces in mechanochemical reactions based on a rational design of the mechanophore and its surrounding. The basis for this will be a careful benchmark of computational methods against experimental data, with the aim of identifying a computational protocol that yields reliable and physically sound results for the calculation of the mechanochemical rupture forces in diverse processes.

In the second phase of the project OEEFs will be applied in combination with mechanical forces to evaluate in how far an OEEF with a certain strength and orientation decreases the rupture force of a mechanophore in a mechanochemical process. Another careful benchmark will be carried out, this time with the focus on the correct reproduction of molecular properties in strong electric fields. Since most density functionals are error-prone when treating charge-transfer processes and this property can be expected to be aggravated in the presence of a strong external electric field, the results obtained via Density Functional Theory (DFT) will be regarded with great caution. Subsequently, a number of mechanochemical processes reported in literature will be investigated, including Diels-Alder reactions and scission/recombination events in self-healing materials, with applied external electric fields of different strengths and orientations.

For the major part of the calculations conducted

in the course of this project the Q-Chem program package will be 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 Judgement of Energy DIstribution (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 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 will be applied to model both effects simultaneously, thus paving the way for experimental verification.

WWW

<https://www.uni-bremen.de/en/stauch-group/>

More Information

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