

Force-induced reversal of β -eliminations : stressed disulfide bonds in alkaline solution.

Autorzy

Przemysław Dopieralski

Jordi Ribas-Arino

Padmesh Anjukandi

Martin Krupička

Dominik Marx

Rok wydania

2016

Czasopismo

Angewandte Chemie -
International Edition

Numer woluminu

55

Strony

1304-1308

DOI

10.1002/anie.201508005

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Understanding the impact of tensile forces on disulfide bond cleavage is not only crucial to the breaking of cross-linkers in vulcanized materials such as strained rubber, but also to the regulation of protein activity by disulfide switches. By using ab initio simulations in the condensed phase, we investigated the response of disulfide cleavage by β -elimination to mechanical stress. We reveal that the rate-determining first step of the thermal reaction, which is the abstraction of the β -proton, is insensitive to external forces. However, forces larger than about 1 nN were found to reshape the free-energy landscape of the reaction so dramatically that a second channel is created, where the order of the reaction steps is reversed, turning β -deprotonation into a barrier-free follow-up process to C–S cleavage. This transforms a slow and force-independent process with second-order kinetics into a unimolecular reaction that is greatly accelerated by mechanical forces.

Słowa kluczowe

computational chemistry, mechanochemistry, elimination, molecular dynamics, reaction mechanisms

Adres publiczny

<http://dx.doi.org/10.1002/anie.201508005>

Strona internetowa wydawcy

onlinelibrary.wiley.com