On the overwhelming complexity of mechanochemical disulphide bond reduction in alkaline solution.

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Streszczenie

The coupling between mechanical stress and the reactivity of disulphide bridges has recently received a great deal of attention due to its broad relevance in biochemistry and materials science. Here, we will highlight the main findings of our computational studies on mechanochemistry of disulphide bridges, which have been carried out in the past few years in the framework of GCS Large Scale Projects. Our investigations have disclosed a very complex mechanistic scenario for the mechanochemistry of disulphides in aqueous alkaline solution. In the low-force regime, external forces play a dual role in the reduction of disulphide bridges via a bimolecular SN 2 attack of a hydroxide ion at a sulphur atom. On the one hand, the external tensile force accelerates the reaction by virtue of the mechanical work performed on the system as the reaction proceeds. On the other hand, tensile forces can induce a conformational distortion of the disulphide moiety that drives the system into a spatial arrangement that is less prone to a nucleophilic attack due to steric hindrance. In the high-force regime, in turn, the tensile force gives rise to a competition between bimolecular SN 2 and unimolecular C–S bond breaking mechanisms as well as to drastic changes in the free energy landscape of the system as a result of which bimolecular reaction pathways transform into pure bond-breaking processes. Our results not only provide a rationale for the enigmatic outcome of certain single-molecule force spectroscopy experiments but also suggest new experiments to continue unravelling the intricacies of the mechanochemistry of disulphide bridges.