Unexpected mechanochemical complexity in the mechanistic scenarios of disulfide bond reduction in alkaline solution.

Autorzy

Przemysław Dopieralski

Jordi Ribas-Arino

Padmesh Anjukandi

Martin Krupička

Dominik Marx

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The reduction of disulfides has a broad importance in chemistry, biochemistry and materials science, particularly those methods that use mechanochemical activation. Here we show, using isotensional simulations, that strikingly different mechanisms govern disulfide cleavage depending on the external force. Desolvation and resolvation processes are found to be crucial, as they have a direct impact on activation free energies. The preferred pathway at moderate forces, a bimolecular S_N2 attack of OH^- at sulfur, competes with unimolecular C–S bond rupture at about 2 nN, and the latter even becomes barrierless at greater applied forces. Moreover, our study unveils a surprisingly rich reactivity scenario that also includes the transformation of concerted S_N2 reactions into pure bond-breaking processes at specific forces. Given that these forces are easily reached in experiments, these insights will fundamentally change our understanding of mechanochemical activation in general, which is now expected to be considerably more intricate than previously thought.

Adres publiczny

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