

Mechanism of Conformational Flexibility at the Disulfide Bond: Role of Singlet Oxygen Addition and Elimination

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ABSTRACT

A density functional theory study is presented that provides the evidence that singlet oxygen ($^1\text{O}_2$) has a path to engage in reversible bonding with RS-SR . This path can promote rotation about the S-S bond. Mechanistic detail provided by this study reveals a $^1\text{O}_2$ -induced conformational easing process, which enables greater flexibility prior to departure of molecular oxygen. The role $^1\text{O}_2$ plays in enhancing conformational flexibility from reversible interactions with alkenes and polyenes has been studied, but is overlooked with disulfides. Disulfides allow for an addition of singlet oxygen to yield a persulfoxide [$\text{RSS}^+(\text{-OO}^-)\text{R}$] that in one path leads to oxygen departure. Insight is provided for a conformation relaxation process about the S-S bond prior to departure as $^1\text{O}_2$ or $^3\text{O}_2$.

