

Novel Rearrangement of Alkyl Trisulfides to Thiono-Disulfides: A Computational Investigation

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Dimethyl trisulfide (DMTS) has been shown to convert cyanide to thiocyanate both through direct reaction and vis-à-vis an enzymatic reaction involving rhodanese, a sulfurtransferase known to convert cyanide to thiocyanate *in vivo* and *in vitro*. Based on this chemistry, we sought to rationalize these reactions through a common chemical intermediate. Work done at the DFT level supports the hypothesis that DMTS undergoes a novel, single-step rearrangement to a thiono disulfide (CS(S)SC in SMILES notation). The DFT results were supported by calculations performed at the CCSD level of theory. An interesting consequence of this work was that perturbation theory (MP2 and MP3) was shown to be incapable of properly describing the potential energy surface of the hypervalent sulfur species resulting from the rearrangement of DMTS. Further work is underway to determine if molecules containing hypervalent atoms pose a significant challenge to accurate description by perturbation theory.