Beckmann rearrangement of cyclohexanone-oxime into ε-caprolactam in supercritical water

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A figure of merit of supercritical water (SCW) is its ability of accelerating synthetic organic reactions. In this respect, it represents a viable possibility to replace the standard highly concentrated acid catalyst, environmentally harmful. In an attempt to understand the mechanism behind this observation, we analyze, via first principles molecular dynamics, the Beckmann rearrangement of cyclohexanone-oxime into ε-caprolactam in SCW, for which accurate experimental evidence has been reported. The simulation shows that the reaction depends on the dynamical nature of the hydrogen bonding at supercritical conditions and on the density of SCW. The active participation of the surrounding solvent is crucial not only in enhancing the initial step of the reaction, but also in driving the pathway towards the desired channel by both hydrolysis of single H₂O monomers and proton exchange mechanisms between the solute and the solvent.