

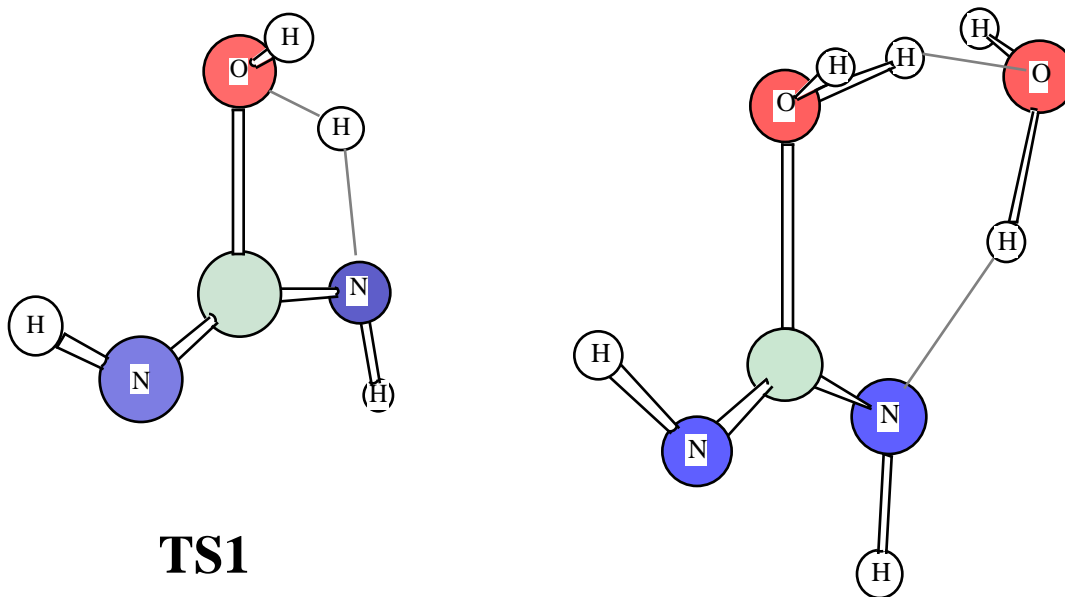
NUCLEOPHILIC ADDITIONS TO CUMULENES: “WATER CATALYSIS” OF THE HYDROLYSIS OF THE PARENT CARBODIIMIDE.

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The hydration of the parent carbodiimide has been studied with higher level ab initio methods. Thermodynamic and kinetic parameters have been determined at various levels of Gaussian theory (G1, G2, G2MP2, G2MP3). The G2 model is the best and intended to approximate QCISD(T)/6-311+G(3df,2p) calculations which we also have computed directly. The hydrolysis is a two-step process that involves the rate-limiting addition of water across one C=N bond followed by a tautomerization leading to urea. This presentation will focus on the effects of “water catalysis” on both steps of the reaction path.



The G2 calculations approximate the QCISD(T)/6-311+G(3df,2p) calculations quite well for the loosely bound pre-coordination complex, and for the two transition states. However, the G2 approximation is found to be markedly less accurate as far as the reaction energies are concerned and G2 values may differ by as much as 10 kcal/mol from the QCISD(T) values they approximate. Comparisons are made to additions to isoelectronic species (ketenes, CO₂) and to the related heteroalkenes. Chemical and biological implications are discussed.