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To bridge or not to bridge: The role of sulfuric acid in the Beckmann rearrangement

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ABSTRACT

Based on ab initio calculations using the Gaussian-4 method, we propose a new catalytic mechanism for the Beckmann rearrangement in concentrated H_2SO_4. Our calculations suggest that H_2SO_4 catalyzes the 1,2-proton-shift step via a cyclic transition structure, in which H_2SO_4 acts as a proton-transfer bridge. The reaction barrier for this mechanism is lower by 48.1 kJ/mol than the barrier for the previously suggested catalytic mechanism, which involves a strained 3-memberd-ring transition structure. According to the previous mechanism the 1,2-proton shift has the highest activation energy, while in the revised mechanism the highest activation energy is obtained for the ensuing rearrangement/dehydration step.

Keywords: Beckmann rearrangement, H_2SO_4 catalyst, CCSD(T), G4 theory.