The mechanism of the gas-phase elimination kinetics of the β,γ-unsaturated aldehyde 2,2–dimethyl-3-butenal: a theoretical study

Rodriguez, Andrea Cartaya; Loriett Maldonado, Alexis; Mora, Jose R.; Marquez Brazon, Edgar Alexander; Córdova, Tania C.; Chuchani, Gabriel.

Abstract

The study on the mechanism of the gas-phase elimination or thermal decomposition kinetics of 2, 2-dimethyl-3-butenal has been carried out by using theoretical calculation at MP2, combined ab initio CBSQB3 and DFT (B3LYP, B3PW91, MPW1PW91, PBEPBE, PBE1PBE, CAMB3LYP, M06, B97d) levels of theory. A good reasonable agreement between experimental and calculated parameters was obtained by using CAMB3LYP/6-311G(d,pd) calculations. The contrasted calculated parameters against experimental values suggested decarbonylation reaction to proceed through a concerted five-membered cyclic transition state type of mechanism, involving the hydrogen transfer from the carbonyl carbon to the gamma carbon, consistent with observed kinetic isotope effect. The breaking of alpha carbon–carbonyl carbon bond to produce carbon monoxide is 50% advanced in the transition state. The reaction mechanism may be described as a concerted moderately non-synchronous process. Examination of the Atoms in Molecules (AIM) analysis of electron density supports the suggested mechanism.

keywords

2,2-dimethyl-3-butenal, elimination, kinetic, mechanism, Theoretical calculation.