Theoretical study of the thermolysis reaction of Ethyl ?-hydroxycarboxylates in the gas phase

Notario, Rafael

Quijano, Jairo

Camilo Quijano, J.

Gutiérrez, Luisa P.

Suárez, Wilmar A.

Sánchez, Claudia

León, Luis A.

Chamorro, Eduardo

Theoretical studies on the thermolysis of three ethyl ?-hydroxycarboxylates in the gas phase were carried out using ab initio theoretical methods, at the MP2/6-31G(d) and MP2/6-311++G(2d,p)//MP2/6-31G(d) levels of theory. Two competitive reaction pathways for the decomposition process have been studied. The first pathway describes a two-step mechanism, with the formation in a first step of an aldehyde, or a ketone, and an enol intermediate, followed by the tautomerization of this intermediate to ethyl acetate. The second pathway is a one-step mechanism with formation of ethylene and a carboxylic acid. Both processes occur via six-membered cyclic transition states. The thermolysis is favorable along the first pathway with the first step as the rate-limiting step for the global process. The progress of the principal reactions was followed by means of the Wiberg bond indices. The results indicate that the transition states are late, and the calculated synchronicities show that the reactio